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(54) [Title of the Invention] CURABLE COMPOSITION

(57) [Abstract]

[Object] To provide a curable composition capable of more certainly preventing the generation of cracks, whitening or the like over a long time, irrespective of whether the cured product is a thick film or a thin film.

[Construction] A curable composition comprising: (A) an oxyalkylene polymer having a group of the formula (1):

$$-SiX_aR^1_{(3-a)} \qquad (1)$$

[wherein R^1 is a monovalent organic group; X is a hydroxyl group or a hydrolyzable group; and a is from 1 to 3], (B) a polymer containing a (meth)acrylic acid alkyl ester monomer unit, and (C) a macromolecular plasticizer having an average molecular weight of 1000 or more.

[CLAIMS]

[Claim 1]

A curable composition comprising: (A) an oxyalkylene polymer having a reactive silicon group represented by the following formula (1):

$$-SiX_aR^1_{(3-a)} \qquad (1)$$

[wherein R^1 represents a monovalent organic group having 1 to 20 carbon atoms which may be substituted; X represents a hydroxyl group or a hydrolyzable group; and a represents an integer from 1 to 3, provided that when a plurality of R^1 is present, R^1 may be identical with or different from each other, and when a plurality of X is present, X may be identical with or different from each other],

(B) a polymer containing a (meth)acrylic acid alkyl ester monomer unit, and (C) a macromolecular plasticizer having an average molecular weight of 1000 or more.

[Claim 2]

The curable composition according to claim 1, wherein at least a part of the macromolecular plasticizer (C) is composed of an oxyalkylene polymer which does not have the reactive silicon group represented by the formula (1).

[Claim 3]

The curable composition according to claim 1 or 2, wherein the macromolecular plasticizer (C) has a viscosity of 5 Pa·s or less at 25°C.

[Claim 4]

The curable composition according to any one of claims

1 to 3, wherein the oxyalkylene polymer (A) has a viscosity of 20 Pa·s or less at 25°C.

[Claim 5]

The curable composition according to any one of claims 1 to 4, wherein the polymer (B) is a polymer containing, as the (meth)acrylic acid alkyl ester monomer unit, a (meth)acrylic acid alkyl ester monomer unit having an alkyl group having 1 to 8 carbon atoms, and a (meth)acrylic acid alkyl ester monomer unit having an alkyl group having 10 or more carbon atoms.

[Claim 6]

The curable composition according to any one of claims 1 to 5, wherein the polymer (B) is a polymer containing a (meth)acrylic acid alkyl ester monomer unit and also having the reactive silicon group represented by the formula (1).

[Detailed Description of the Invention]

[0001]

[Industrial Field of the Invention]

The present invention relates to a curable composition, and more particularly, to a moisture-curable type curable composition which is suitable as a main component for sealants, adhesives and the like.

[0002]

[Related Art]

An oxyalkylene polymer having a reactive silicon group such as an alkoxysilyl group (hereinafter, referred to as curable oxyalkylene polymer) can be cured even at room

temperature under the action of the moisture in air, and after being cured, the oxyalkylene polymer gives a cured product having rubber elasticity, and has excellent adhesiveness to various objects to be adhered. Therefore, oxyalkylene polymers are widely used as a main agent for sealants, adhesives, and compositions for coating or sealing, or the like.

[0003]

In recent years, there have been attempts to modify those curable oxyalkylene polymers, by a method of mixing a polymer of an unsaturated group-containing monomer such as a (meth)acrylic acid alkyl ester monomer, with such a curable oxyalkylene polymer, or a method of polymerizing the unsaturated group-containing monomer in the presence of the curable oxyalkylene polymer. These attempts are disclosed in, for example, Japanese Patent Application Laid-Open (JP-A) No. 59-78223, JP-A No. 59-122541, JP-A No. 60-31556, JP-A No. 63-112642, JP-A No. 1-275648, JP-A No. 6-172631, WO 98/47937 and the like, and it is reported that such modifications make it possible to improve the mechanical properties, weather resistance, coating adherence, and the like.

[0004]

[Problems to be Solved by the Invention]

However, the inventors of the present invention found that a curable oxyalkylene polymer modified with a polymer of an unsaturated group-containing monomer such as a (meth)acrylic acid alkyl ester monomer (hereinafter, referred to as acrylic polymer-modified curable oxyalkylene polymer), as disclosed in

the publications mentioned above, is still unsatisfactory in terms of weather resistance in a situation where the polymer is exposed to more severe conditions. That is, the inventors found that under the conditions such as being exposed to wind and rain, sunlight or the like due to outdoor weathering, if the duration of weathering is increased, the cured products have cracks or whitening, and particularly, generation of such defects becomes significant as the film thickness of the cured product is decreased.

[0005]

The present invention was made in view of such problems of the related art, and it is an object of the present invention to provide a curable composition which is capable of more certainly preventing the generation of cracks, whitening or the like over a long time, irrespective of whether the cured product is a thick film or a thin film.

[0006]

[Means for Solving the Problems]

The inventors of the present invention extensively conducted research in order to achieve the object described above, and as a result, they found that when a compound which is generally known as a macromolecular plasticizer and has a molecular weight of a certain value or more, is added to an acrylic polymer-modified curable oxyalkylene polymer, a curable composition may be obtained, which is capable of more certainly preventing the generation of cracks, whitening or the like over a long time, irrespective of whether the cured product

is a thick film or a thin film. Thus, the inventors completed the present invention.

[0007]

Adding a macromolecular plasticizer to a curable oxyalkylene polymer which has not been subjected to modification by an acrylic polymer, is a known technology as is disclosed in, for example, JP-A No. 1-171683, JP-A No. 1-279958, JP-A No. 5-287189, JP-A No. 5-339490, JP-A No. 7-113049, JP-A No. 9-194735, and JP-A No. 10-60253. However, with regard to the compositions specified in the above publications, the effect obtainable by the addition of a macromolecular plasticizer in addition to a plasticizing effect was limited only to enhancements in fouling resistance, storage stability and coating dryability, or the like.

[0008]

On the other hand, the inventors of the present invention found that the macromolecular plasticizer offers an effect that is conventionally not known at all, which relates to an enhancement of weather resistance over a long time in a combination with an acrylic polymer-modified curable oxyalkylene polymer. The inventors also found that this enhancement of weather resistance lasts longer and far surpasses the weather resistance of acrylic polymer-modified curable oxyalkylene polymers that are not added with macromolecular plasticizer.

[0009]

That is, the curable composition of the present invention

is characterized by containing (A) an oxyalkylene polymer having a reactive silicon group represented by the following formula (1):

$$-SiX_aR^1_{(3-a)} \qquad (1)$$

[wherein R^1 represents a monovalent organic group having 1 to 20 carbon atoms which may be substituted; X represents a hydroxyl group or a hydrolyzable group; and a represents an integer from 1 to 3, provided that when a plurality of R^1 is present, R^1 may be identical with or different from each other, and when a plurality of X is present, X may be identical with or different from each other], (B) a polymer containing a (meth)acrylic acid alkyl ester monomer unit, and (C) a macromolecular plasticizer having an average molecular weight of 1000 or more.

[0010]

According to the present invention, it is preferable that at least a part of the macromolecular plasticizer (C) be composed of an oxyalkylene polymer which does not have the reactive silicon group represented by the formula (1). Furthermore, it is preferable for the macromolecular plasticizer (C) to have a viscosity of 5 Pa·s or less at 25°C, and it is preferable for the oxyalkylene polymer (A) to have a viscosity of 20 Pa·s or less at 25°C.

[0011]

According to the present invention, it is preferable that the polymer (B) be a polymer containing, as the (meth)acrylic acid alkyl ester monomer unit, a (meth)acrylic acid alkyl ester

monomer unit having an alkyl group having 1 to 8 carbon atoms and a (meth)acrylic acid alkyl ester monomer unit having an alkyl group having 10 or more carbon atoms. It is also preferable that the polymer (B) be a polymer which contains a (meth)acrylic acid alkyl ester monomer unit and has the reactive silicon group represented by the formula (1).

[0012]

[Embodiments]

The curable composition of the present invention contains (A) an oxyalkylene polymer having a reactive silicon group represented by the following formula (1):

$$-SiX_aR^1_{(3-a)} \qquad (1)$$

[wherein R^1 represents a monovalent organic group having 1 to 20 carbon atoms which may be substituted; X represents a hydroxyl group or a hydrolyzable group; and a represents an integer from 1 to 3, provided that when a plurality of R^1 is present, R^1 may be identical with or different from each other, and when a plurality of X is present, X may be identical with or different from each other], (B) a polymer containing a (meth)acrylic acid alkyl ester monomer unit, and (C) a macromolecular plasticizer having an average molecular weight of 1000 or more.

[0013]

First, the oxyalkylene polymer (A) according to the present invention will be described. The oxyalkylene polymer (A) according to the present invention is an oxyalkylene polymer having the reactive silicon group which includes a hydroxyl

group or a hydrolyzable group. In the present invention, the hydrolyzable group means a group which can undergo a hydrolysis reaction and produce a hydroxyl group. Therefore, examples of the hydrolyzable group include a halogen atom, an alkoxy group, an acyloxy group, an alkenyloxy group, an amino group, a ketoximate group, an aminooxy group, a carbamoyl group, and a mercapto group.

[0014]

The halogen atom is preferably a chlorine atom, and the alkoxy group is preferably an alkoxy group having 1 to 6 carbon atoms. It is more preferable that the alkoxy group have 1 to 4 carbon atoms, and examples of such a group include a methoxy group, an ethoxy group, a propoxy group and a butoxy group. The acyloxy group may be, for example, an acetoxy group, while the alkenyloxy group may be, for example, a propenoxy group. The amino group is preferably an N-substituted amino group, and is more preferably an N,N-dialkylamino group such as an N,N-dimethylamino group. The carbamoyl group is preferably an N-substituted carbamoyl group such as an N-methylcarbamoyl group. The ketoximate group may be, for example, an acetoximate group or a dimethylketoximate group.

[0015]

According to the present invention, since the reactive silicon group is used in the crosslinking of the oxyalkylene polymer, it is preferable that the reactivity of the hydrolyzable group in the reactive silicon group be mild, and it is also preferable that the molecule leaving as a result of

a hydrolysis reaction be a volatile small molecule which is capable of diffusing in air without being entrapped in the oxyalkylene polymer molecule. From a standpoint as such, in the present invention, the hydrolyzable group is preferably an alkoxy group, and most preferably a methoxy group.

[0016]

The reactive silicon group has one to three hydrolyzable groups or hydroxyl groups such as explained above, and when the total number of these groups is 1 or 2, the silicon atom in the reactive silicon group has two or one group R^1 bound thereto. This R^1 is a monovalent organic group having 1 to 20 carbon atoms, and the relevant organic group may be substituted or unsubstituted, but is preferably unsubstituted. According to the present invention, when the carbon number of R^1 exceeds 20, since a bulky organic group is present in the reactive silicon group, the reactivity of the hydrolyzable group or hydroxyl group in the reactive silicon group described above becomes insufficient. According to the present invention, R^1 preferably has 1 to 16 carbon atoms, and more preferably 1 to 8 carbon atoms.

[0017]

When R^1 is an unsubstituted monovalent organic group, the structure is not particularly limited, and R^1 may have any of a linear structure, a branched structure and a cyclic structure. Examples of such an organic group include an alkyl group, a cycloalkyl group, an aryl group, and an aralkyl group. The alkyl group is preferably an alkyl group having 1 to 4 carbon

atoms, and examples of such an alkyl group include a methyl group, an ethyl group, a propyl group, and a butyl group. Furthermore, when R^1 is a substituted monovalent organic group, the type of the substituent is not particularly limited.

[0018]

In regard to the reactive silicon group, when a plurality of the groups represented by X or the organic group R^1 is present, those groups may be respectively identical with or different from each other. Also, from the viewpoint of promoting the crosslinking of the oxyalkylene polymer, it is preferable that the number of X (represented by a in the formula (1)) be 2 or 3. Since the group R^1 such as described above is preferably a non-bulky group, and the hydrolyzable group is preferably a methoxy group, it is particularly preferable for the present invention that the reactive silicon group be a methyldimethoxysilyl group or a trimethoxysilyl group.

[0019]

The oxyalkylene polymer (A) according to the present invention is a compound having the reactive silicon group represented by the formula (1) explained above, in the molecule of an oxyalkylene polymer. Here, the number of reactive silicon groups per molecule of the oxyalkylene polymer, or binding sites of the reactive silicon groups in the oxyalkylene polymer are not particularly limited. That is, the oxyalkylene polymer (A) may have one or more reactive silicon groups per molecule, and the sites of presence may be at the termini of the oxyalkylene polymer or at a side chain, or at both the termini and the side

chain.

[0020]

Furthermore, the oxyalkylene polymer having the reactive silicon group is desirably a polymer having oxyalkylene as a repeating unit, and the oxyalkylene may consist of only one kind, or may consist of two or more kinds. Particularly, when the oxyalkylene polymer is composed of two or more kinds of oxyalkylene repeating units, the respective oxyalkylenes may be randomly linked to form a random polymer of oxyalkylene, or oxyalkylene units of the same kind may be linked in a block shape so that those blocks form a block copolymer.

[0021]

The oxyalkylene polymer may also have, within the molecule, a chemical structure other than the oxyalkylene as a repeating unit. As will be described later, since it is general to synthesize the oxyalkylene polymer by reacting an initiator (initiator) with a cyclic ether, the oxyalkylene polymer may have a functional group derived from an initiator in the molecule. Furthermore, as will be described later, since the oxyalkylene polymer is often subjected to molecular weight increase, by allowing the hydroxyl group contained in the polymer to react with another functional group, the oxyalkylene polymer may have a bond produced by the reaction between the hydroxyl group and the other functional group (for example, a urethane bond or the like) in the molecule.

[0022]

The oxyalkylene polymer (A) according to the present

invention is preferably obtained by using an oxyalkylene polymer having a functional group as a raw material, and reacting a part or all of the functional groups with a compound having the reactive silicon group represented by the formula (1). In this case, the reactive silicon group represented by the formula (1) is preferably linked to the oxyalkylene polymer via a divalent organic group. When the reactive silicon group is linked to the oxyalkylene polymer via a divalent organic group, the reactive silicon group acquires a structure represented by the following formula (2):

$$-R^0-SiX_aR^1_{(3-a)} \qquad (2)$$

[wherein R^0 represents a divalent organic group; and R^1, X and a have the same meanings as previously defined for R^1, X and a].

[0023]

As the oxyalkylene polymer having a functional group, which is used as a raw material for the production of the oxyalkylene polymer (A) according to the present invention, there may be mentioned an oxyalkylene polymer having a hydroxyl group, an unsaturated group or an isocyanate group as the functional group. The type of the functional group is not limited to these, and any functional group which is capable of reacting with a compound having the reactive silicon group and introducing the reactive silicon group into the oxyalkylene polymer, can all be used. The number or position of the functional groups in the oxyalkylene polymer is also not particularly limited, and a compound in which one or two or more

kinds of functional groups are bound to the termini and/or side chain of the oxyalkylene polymer, can be used.

[0024]

According to the present invention, it is preferable to use an oxyalkylene polymer having a hydroxyl group at the termini (hereinafter, referred to as hydroxyl group-terminated oxyalkylene polymer), as the oxyalkylene polymer having a functional group. This is because an oxyalkylene polymer having another functional group is relatively easily obtained by converting the terminal hydroxyl group of the hydroxyl group-terminated oxyalkylene polymer into another functional group.

[0025]

The hydroxyl group-terminated oxyalkylene polymer can be obtained by subjecting a cyclic ether such as ethylene oxide, propylene oxide, 1,2-butylene oxide, 2,3-butylene oxide or tetrahydrofuran to ring-opening polymerization, using an active hydrogen-containing compound such as a monohydric or polyhydric alcohol or a monovalent or polyvalent carboxylic acid as an initiator. In this case, an alkali metal catalyst such as a potassium-based compound or a cesium-based compound, a composite metal cyanide complex catalyst, or a metal-porphyrin catalyst can be used as the polymerization catalyst.

[0026]

As the initiator, it is preferable to use a polyvalent active hydrogen-containing compound having 2 to 8 active

hydrogen atoms, and it is more preferable to use a polyvalent active hydrogen-containing compound having 2 to 6 active hydrogen atoms. According to the present invention, since a curable composition having excellent flexibility and adhesiveness after curing is obtained, the number of active hydrogen atoms is even more preferably 2 or 3. As the polyvalent active hydrogen-containing compound, a polyhydric alcohol is preferred.

[0027]

When an alkali metal catalyst is used as the polymerization catalyst for the hydroxyl group-terminated oxyalkylene polymer, a polymer having a relatively low molecular weight is obtained. Thus, the polymer can be subjected to molecular weight increase, by converting the terminal hydroxyl groups of the polymer into sodium alkoxide or the like, and reacting the polymer with a multihalogen compound such as methylene chloride to thereby multimerize the polymer, so that the molecular weight can be increased (see JP-A No. 62-240320). On the other hand, when a composite metal cyanide complex catalyst is used as the polymerization catalyst, a polymer having a high molecular weight and a narrow molecular weight distribution is obtained (see JP-A No. 3-72527).

[0028]

According to the present invention, the polymerization catalyst used to obtain a hydroxyl group-terminated oxyalkylene polymer, is preferably a composite metal cyanide complex catalyst. The composite metal cyanide complex is preferably

a complex having zinc hexacyanocobaltate as a main component, and among others, an ether and/or an alcohol complex are/is preferred. In this case, ethylene glycol dimethyl ether (glyme), diethylene glycol dimethyl ether (diglyme) and the like are preferred as the ether, and from the viewpoint of the handlability at the time of complex production, glyme is particularly preferred. As the alcohol, t-butanol is preferred.

[0029]

The hydroxyl group-terminated oxyalkylene polymer is preferably a divalent to hexavalent polyoxypropylene polyol, and among others, polyoxypropylene diol and polyoxypropylene triol are preferred. The hydroxyl group-terminated oxyalkylene polymer may be a mixture of two or more kinds differing in the molecular weight or chemical structure, and by using such a mixture, adjustment of the properties after curing or adjustment of the curing properties is made possible.

[0030]

When the hydroxyl group-terminated oxyalkylene polymer described above is used, for example, the oxyalkylene polymer (A) having a reactive silicon group can be obtained by the following methods (I) to (IV).

(I) A method of converting the terminal hydroxyl group of the hydroxyl group-terminated oxyalkylene polymer into an unsaturated group, and then reacting the unsaturated group with a hydrosilyl compound.

(II) A method of reacting the hydroxyl group-terminated

oxyalkylene polymer with an isocyanate group-containing silicon compound.

(III) A method of converting the terminal hydroxyl group of the hydroxyl group-terminated oxyalkylene polymer into an isocyanate group, and then reacting the isocyanate group with an active hydrogen-containing silicon compound.

(VI) A method of converting the terminal hydroxyl group of the hydroxyl group-terminated oxyalkylene polymer into an unsaturated group, and then reacting the unsaturated group with a mercapto group-containing silicon compound.

[0031]

According to the method (I), for example, the terminal hydroxyl group of the hydroxyl group-terminated oxyalkylene polymer obtained by the method described above, is reacted with a compound having an unsaturated group and a functional group capable of reacting with a hydroxyl group (hereinafter, referred to as compound 1), whereby the unsaturated group is first introduced into the termini of the oxyalkylene polymer. Examples of the functional group capable of reacting with a hydroxyl group in the compound 1 include those groups capable of forming an ether bond, an ester bond, a urethane bond or a carbonate bond through a reaction with a hydroxyl group. Examples of such a functional group include a halogen atom, a carboxyl group, a haloformyl group, an isocyanate group and the like. Furthermore, examples of the unsaturated group in the compound 1 include an alkenyl group, an acryloyl group, a methacryloyl group and the like. The alkenyl group is

preferably a vinyl group or a group represented by the following formula (3):

$$-R^2-CH=CH_2 \qquad (3)$$

wherein R^2 represents a divalent hydrocarbon group having 1 to 18 carbon atoms.

[0032]

In the group represented by the formula (3), R^2 is preferably a hydrocarbon group having 1 to 5 carbon atoms, and is particularly preferably a methylene group. When R^2 is a methylene group, the group represented by the formula (3) becomes an allyl group. Furthermore, the compound 1 is particularly preferably allyl chloride, and by using this, the terminal hydroxyl group of the oxyalkylene polymer can be easily converted to an allyloxy group.

[0033]

After the unsaturated group is introduced into the termini of the oxyalkylene polymer as described above, the reactive silicon group represented by the formula (1) can be introduced into the termini of the oxyalkylene polymer by allowing the unsaturated group to react with a hydrosilyl compound represented by the following formula (4):

$$HSiX_aR^1_{(3-a)} \qquad (4)$$

wherein R^1, X and a have the same meanings as previously defined R^1, X and a.

[0034]

In the method (I), when the terminal hydroxyl group of the oxyalkylene polymer is converted to an allyloxy group, and

then is reacted with the hydrosilyl compound represented by the formula (4), the terminal hydroxyl group becomes a group represented by the following formula (5):

$$-O-C_3H_6-SiX_aR^1{}_{(3-a)} \qquad (5)$$

wherein R^1, X and a have the same meanings as previously defined for R^1, X and a.

[0035]

In order to make the hydrosilyl compound to react with the oxyalkylene polymer having unsaturated groups at the termini, a catalyst such as a platinum-based catalyst, a rhodium-based catalyst, a cobalt-based catalyst, a palladium-based catalyst and a nickel-based catalyst can be used. The catalyst is preferably a platinum-based catalyst such as chloroplatinic acid, platinum metal, platinum chloride, or a platinum-olefin complex. The hydrosilyl compound is preferably reacted at 30 to 150°C, and preferably at 60 to 120°C, for several hours.

[0036]

According to the method (II), for example, the hydroxyl group-terminated oxyalkylene polymer is reacted with an isocyanate group-containing silicon compound represented by the following formula (6), whereby the reactive silicon group represented by the formula (1) can be introduced into the termini of the oxyalkylene polymer.

$$OCN-R^3-SiX_aR^1{}_{(3-a)} \qquad (6)$$

wherein R^3 represents a divalent hydrocarbon group having 1 to 20 carbon atoms; and R^1, X and a have the same meanings as

previously defined for R^1, X and a.

[0037]

When the terminal hydrogen group in the hydroxyl group-terminated oxyalkylene polymer is reacted with the isocyanate group in the isocyanate group-containing silicon compound represented by the formula (6), a urethane bond is generated, and the reactive silicon group represented by the formula (1) is introduced. In this case, the terminal hydroxyl group of the oxyalkylene polymer becomes a group represented by the following formula (7):

$$-OCONH-R^3-SiX_aR^1_{(3-a)} \qquad (7)$$

wherein R^3, R^1, X and a have the same meanings as previously defined for R^3, R^1, X and a.

[0038]

According to the method (III), for example, the hydroxyl group-terminated oxyalkylene polymer is reacted with a polyisocyanate compound under the conditions in which the number of equivalents of isocyanate is larger than the number of equivalents of hydroxyl group, and thereby, the terminal hydroxyl group of the hydroxyl group-terminated oxyalkylene polymer is first converted to an isocyanate group.

[0039]

Subsequently, the oxyalkylene polymer having isocyanate groups at the termini is reacted with an active hydrogen-containing silicon compound represented by the following formula (8), whereby the reactive silicon group represented by the formula (1) can be introduced into the

termini of the oxyalkylene polymer:

$$W\text{-}R^3\text{-}SiX_aR^1_{(3-a)} \qquad (8)$$

wherein W represents an active hydrogen-containing group selected from the group consisting of a hydroxyl group, a carboxyl group, a mercapto group, a primary amino group and a secondary amino group; and R^3, R^1, X and a have the same meanings as previously defined for R^3, R^1, X and a.

[0040]

As a result of the above reaction, the terminal isocyanate group of the oxyalkylene polymer having isocyanate groups at the termini becomes a group represented by the following formula (9):

$$\text{-}NH\text{-}W^1\text{-}R^3\text{-}SiX_aR^1_{(3-a)} \qquad (9)$$

wherein W^1 represents a divalent group selected from the group consisting of -COO-, -CO-, -COS-, -CONH- and -CONW^2-, provided that W^2 represents a monovalent organic group; and R^3, R^1, X and a have the same meanings as previously defined for R^3, R^1, X and a.

[0041]

According to the method (VI), for example, the termini of the oxyalkylene polymer are first converted to unsaturated groups by the method described in the above section (I), using the hydroxyl group-terminated oxyalkylene polymer. Subsequently, the reactive silicon group represented by the formula (1) can be introduced into the termini of the oxyalkylene polymer, by reacting the oxyalkylene polymer having unsaturated groups at the termini with a mercapto

group-containing silicon compound represented by the following formula (10):

$$HS\text{-}R^3\text{-}SiX_aR^1_{(3-a)} \qquad (10)$$

wherein R^3, R^1, X and a have the same meanings as previously defined for R^3, R^1, X and a.

[0042]

In the method (VI), when the terminal hydroxyl group of the oxyalkylene polymer is converted to an allyloxy group, and then is reacted with the mercapto group-containing silicon compound represented by the formula (10), the terminal hydroxyl group becomes a group represented by the following formula (11):

$$-O\text{-}C_3H_6\text{-}S\text{-}R^3\text{-}SiX_aR^1_{(3-a)} \qquad (11)$$

wherein R^3, R^1, X and a have the same meanings as previously defined for R^3, R^1, X and a.

[0043]

Examples of the mercapto group-containing silicon compound represented by the formula (10) include 3-mercaptopropylmethyldimethoxysilane, 3-mercaptopropyltrimethoxysilane, and the like. Upon carrying out the reaction, a radical polymerization initiator may be used as a radical generating source, and in some cases, the reaction may also be carried out under radiation or heat, without using the radical polymerization initiator. Examples of the radical polymerization initiator include peroxide-based, azo-based or redox-based polymerization initiators or metal compound catalysts. Examples of the radical polymerization initiator include 2,2'-azobisisobutyronitrile,

2,2'-azobis-2-methylbutyronitrile, 2,2'-azobis(2,4-dimethylvaleronitrile), benzoyl peroxide, t-butyl peroxide, acetyl peroxide, diisopropyl peroxydicarbonate, and the like. The above reaction is carried out at 20 to 200°C, and preferably at 50 to 150°C, for several hours to several ten hours.

[0044]

The method (I) is a method involving converting the terminal hydroxyl group of the hydroxyl group-terminated oxyalkylene polymer into an unsaturated group, and then converting the unsaturated group. However, as a modification of this method, the following method is possible.

[0045]

That is, in the case of obtaining the hydroxyl group-terminated oxyalkylene polymer by subjecting a cyclic ether to ring-opening polymerization in the presence of an initiator, an unsaturated bond can be introduced into a side chain of the hydroxyl group-terminated oxyalkylene polymer by using an unsaturated group-containing monoepoxide such as allyl glycidyl ether, glycidyl acrylate or glycidyl methacrylate in combination as the cyclic ether (see JP-A No. 3-79627).

[0046]

Since an oxyalkylene polymer having unsaturated groups at the termini and in a side chain can be obtained by converting the terminal hydroxyl group of this hydroxyl group-terminated oxyalkylene polymer into an unsaturated group in the same manner as in the method (I), an oxyalkylene polymer having the reactive

silicon groups represented by the formula (1) at the termini and in a side chain can be obtained by converting the unsaturated groups in the polymer by a method similar to the method (I).

[0047]

As a modification of the method (I), the following method is also possible. That is, when a compound having an unsaturated group and an active hydrogen group such as allyl alcohol, for example, is use as the active hydrogen-containing compound as an initiator used for obtaining the oxyalkylene polymer, an oxyalkylene polymer having an unsaturated group and terminal hydroxyl groups, such as allyl-terminated polyoxypropylene monool, can be obtained. The terminal hydroxyl groups of the polymer are converted into unsaturated groups by a method similar to the method (I) to thereby convert all of the functional groups of the oxyalkylene polymer into unsaturated groups, and then the reactive silicon group represented by the formula (1) can be further introduced into the oxyalkylene polymer by a method similar to the method (I).

[0048]

The oxyalkylene polymer (A) explained above forms a curable composition, together with (B) a polymer containing a (meth)acrylic acid alkyl ester monomer unit, and (C) a macromolecular plasticizer having an average molecular weight of 1000 or more. This curable composition can be used as a raw material for sealants or elastic adhesives, as will be discussed later. In regard to such applications, since the curable composition should be applied to an object to be adhered before

the curable composition cures, the curable composition requires appropriate workability. Accordingly, it is preferable for the curable composition to have low viscosity at room temperature. Also, it is preferable that after curing, the curable composition have appropriate rupture stress and rupture elongation.

[0049]

Therefore, according to the present invention, the viscosity of the oxyalkylene polymer (A) is preferably 20 Pa·s or less at 25°C, in view of workability. The lower limit of the viscosity is not particularly limited, but is preferably 1 Pa·s or greater, and more preferably 5 Pa·s or greater. If the viscosity of the oxyalkylene polymer (A) exceeds 20 Pa·s, the resulting curable composition tends to have poor workability.

[0050]

Furthermore, according to the present invention, from the viewpoints of rupture stress and rupture elongation of the cured product, the number average molecular weight (Mn) of the oxyalkylene polymer (A) is preferably 6000 to 50000, and more preferably 8000 to 20000. The number average molecular weight according to the present invention means a number average molecular weight (Mn) measured by gel permeation chromatography (GPC) using a tetrahydrofuran solvent and calculated relative to styrene standards. The Mn of the oxyalkylene polymer (A) means the Mn prior to the curing. If the Mn of the oxyalkylene polymer exceeds 50000, for example, in the case of using the

resulting curable composition as a sealant or an elastic adhesive, workability such as extrudability tends to undergo a decrease. On the other hand, when the Mn of the oxyalkylene polymer is less than 6000, the curability of the composition tends to undergo a decrease.

[0051]

The molecular weight distribution of the oxyalkylene polymer (A) can be represented by the ratio of a weight average molecular weight (Mw) and a number average molecular weight (Mn) (Mw/Mn), and the value is preferably 1.0 to 1.7 in the present invention. The ratio Mw/Mn of the oxyalkylene polymer (A) is more preferably 1.0 to 1.6, and even more preferably 1.0 to 1.5. According to the present invention, the ratio Mw/Mn is a ratio of Mw and Mn measured by GPC using a tetrahydrofuran solvent and calculated relative to styrene standards. Here, the ratio Mw/Mn of the oxyalkylene polymer (A) means the ratio of Mw/Mn prior to the curing.

[0052]

When the ratio Mw/Mn of the oxyalkylene polymer (A) exceeds 1.7, the resulting curable composition tends to have a decreased rate of curing. This is because the oxyalkylene polymer (A) tends to have a slow rate of curing as the molecular weight is smaller. That is, when a comparison is made between oxyalkylene polymers (A) having an identical average molecular weight, with one having a value of Mw/Mn of 1.0 to 1.7 and the other having a value of Mw/Mn of greater than 1.7, the polymer having a value of Mw/Mn of greater than 1.7 has a broad molecular

weight distribution, and thus the content of low molecular weight components is high. For that reason, the rate of curing tends to decrease. An oxyalkylene polymer (A) having a narrow molecular weight distribution, with the value of Mw/Mn being 1.0 to 1.7, can be obtained by using the aforementioned composite metal cyanide complex as the cyclic ether ring-opening polymerization catalyst.

[0053]

Next, the polymer (B) containing a (meth)acrylic acid alkyl ester monomer unit in the curable composition of the present invention will be explained. The polymer (B) according to the present invention desirably contains a (meth)acrylic acid alkyl ester monomer unit as an essential component, and the polymer may be a polymer containing only the (meth)acrylic acid alkyl ester monomer unit, or may be a polymer containing the (meth)acrylic acid alkyl ester monomer unit and an additional unsaturated group-containing monomer unit. Here, the polymer containing a (meth)acrylic acid alkyl ester monomer unit means a polymer having a repeating unit formed from a (meth)acrylic acid alkyl ester, and this polymer can be obtained usually by polymerizing unsaturated group-containing monomers which include a (meth)acrylic acid alkyl ester monomer as an essential component. According to the present invention, the unsaturated group-containing monomer means a compound which has an unsaturated bond (preferably, a carbon-carbon double bond) and is capable of forming a polymer, and the (meth)acrylic acid alkyl ester refers to an acrylic acid alkyl ester or a

methacrylic acid alkyl ester.

[0054]

The (meth)acrylic acid alkyl ester monomer according to the present invention can be represented by the following formula (12):

$$CH_2{=}CR^4COOR^5 \qquad (12)$$

wherein R^4 represents a hydrogen atom or a methyl group; and R^5 represents an alkyl group.

[0055]

R^5 in the formula (12) is an alkyl group, but as in the case of the aralkyl group, cycloalkylalkyl group or the like in the present invention, a substituted alkyl group such as one having at least one hydrogen atom of the alkyl group substituted by a hydrocarbon group such as a cyclic hydrocarbon group, is also intended to be included in the alkyl group. The carbon number of the alkyl group is not particularly limited.

[0056]

The polymer (B) according to the present invention may be a polymer having repeating units composed of one or two or more kinds of (meth)acrylic acid alkyl ester monomers such as represented by the formula (12), or may be a polymer having repeating units composed of one or two or more kinds of (meth)acrylic acid alkyl ester monomers such as represented by the formula (12) and one or two or more kinds of unsaturated group-containing monomers other than the foregoing monomer. In regard to the limitation on the repeating units formed from the (meth)acrylic acid alkyl ester monomer, the type or number

of the repeating units in the polymer (B) is not particularly limited. Furthermore, the proportion of the (meth)acrylic acid alkyl ester monomers in all of the monomers is preferably greater than 50% by mass, and more preferably 70% by mass or more.

[0057]

According to the present invention, it is preferable that the polymer (B) be a polymer containing a (meth)acrylic acid alkyl ester monomer unit having an alkyl group having 1 to 8 carbon atoms and a (meth)acrylic acid alkyl ester monomer unit having an alkyl group having 10 or more carbon atoms, as the (meth)acrylic acid alkyl ester monomer units. That is, the polymer (B) preferably has both the repeating unit formed from the (meth)acrylic acid alkyl ester monomer having an alkyl group having 1 to 8 carbon atoms and the repeating unit formed from the (meth)acrylic acid alkyl ester monomer having an alkyl group having 10 or more carbon atoms. When such a combination is used as the (meth)acrylic acid alkyl ester monomer, the compatibility of the polymer (B) with the oxyalkylene polymer (A) is enhanced, and therefore, the properties of the resulting curable composition, such as strength after curing, tend to be enhanced. As the (meth)acrylic acid alkyl ester monomer having the alkyl group having 10 or more carbon atoms, a (meth)acrylic acid alkyl ester monomer having an alkyl group having 10 to 30 carbon atoms is more preferred, and a (meth)acrylic acid alkyl ester monomer having an alkyl group having 10 to 22 carbon atoms is even more preferred.

[0058]

Examples of the (meth)acrylic acid alkyl ester monomer having the alkyl group having 1 to 8 carbon atoms include methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, hexyl (meth)acrylate, octyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, and benzyl (meth)acrylate.

[0059]

Examples of the (meth)acrylic acid alkyl ester monomer having the alkyl group having 10 or more carbon atoms include decyl (meth)acrylate, dodecyl (meth)acrylate, tetradecyl (meth)acrylate, hexadecyl (meth)acrylate, octadecyl (meth)acrylate, eicosanyl (meth)acrylate, docosanyl (meth)acrylate, and hexacosanyl (meth)acrylate.

[0060]

In the case of using the (meth)acrylic acid alkyl ester monomer having the alkyl group having 1 to 8 carbon atoms and the (meth)acrylic acid alkyl ester monomer having an alkyl group having 10 or more carbon atoms in combination, the ratio is not particularly limited, but the mass ratio of the former/the latter is preferably 95/5 to 40/60, and more preferably 95/5 to 40/60.

[0061]

The polymer (B) according to the present invention may also contain, in addition to the (meth)acrylic acid ester monomer unit, an unsaturated group-containing monomer unit other than the relevant monomer unit. As the unsaturated

group-containing monomer other than the (meth)acrylic acid alkyl ester monomer, a compound represented by the following formula (13) may be mentioned, but is not limited to thereto:

$$CH_2{=}CR^4COOR^6 \qquad (13)$$

wherein R^6 represents a monovalent organic group excluding an alkyl group, or a hydrogen atom; and R^4 has the same meaning as previously defined for R^4.

[0062]

In the formula (13), the monovalent organic group excluding an alkyl group means a monovalent organic group excluding the alkyl group defined for the formula (12). Examples of such a monovalent organic group include monovalent groups containing an alkyl group having a substituent other than a hydrocarbon group (a halogen atom, a hydroxyl group, an isocyanate group, a phenoxy group, a furfuryl group, a reactive silicon group or the like), a glycidyl group or a polyalkylene glycol, and the like. Specific examples of the compound represented by the formula (13) include (meth)acrylic acid; hydroxyalkyl (meth)acrylates such as hydroxyethyl (meth)acrylate; isocyanatoalkyl (meth)acrylates such as isocyanatoethyl (meth)acrylate; phenoxyalkyl (meth)acrylates such as 2-phenoxyethyl (meth)acrylate; (meth)acrylates having a (hydrogenated) furfuryl group, such as furfuryl (meth)acrylate and tetrahydrofurfuryl (meth)acrylate; (meth)acryloxyalkylalkoxysilanes such as γ-(methacryloxypropyl)trimethoxysilane; glycidyl (meth)acrylate; (meth)acrylic acid esters of polyalkylene

oxide monools, such as methoxypolyethylene glycol (meth)acrylate; and the like.

[0063]

As the unsaturated group-containing monomer, compounds listed below can also be used, in addition to the compound represented by the formula (13). That is, N-substituted or N,N-substituted (meth)acrylamides such as N,N-dimethylacrylamide; unsaturated glycidyl ethers such as vinyl glycidyl ether, allyl glycidyl ether and methallyl glycidyl ether; glycidyl esters of unsaturated monocarboxylic acids, such as glycidyl crotonate, glycidyl cinnamate and glycidyl vinylbenzoate; monoalkyl monoglycidyl esters or diglycidyl esters of unsaturated dicarboxylic acids; styrene-based monomers such as styrene, α-methylstyrene and chlorostyrene; cyano group-containing monomers such as acrylonitrile and 2,4-dicyanobutene-1; vinyl ester-based monomers such as vinyl acetate and vinyl propionate; diene-based monomers such as butadiene, isoprene and chloroprene; olefins; halogenated olefins; unsaturated esters; vinyl ethers; and the like can be used.

[0064]

The method for producing the polymer (B) according to the present invention is not particularly limited. To take an example of using the aforementioned unsaturated group-containing monomers which include the (meth)acrylic acid alkyl ester monomer as an essential component, polymerization can be achieved by radical polymerization, anionic

polymerization, cationic polymerization or the like. The polymer (B) according to the present invention is preferably polymerized by radical polymerization, and the mode of polymerization may be any of solution polymerization, emulsion polymerization, suspension polymerization and bulk polymerization.

[0065]

In the case of performing radical polymerization in the present invention, a radical polymerization initiator is usually added to the unsaturated group-containing monomer as a radical generating source. The radical polymerization initiators that can be used in the present invention are as described above. In the case of carrying out activation by means of radiation or heat, the radical initiator is not necessarily needed. The reaction is preferably carried out at 20 to 200°C (preferably, 50 to 150°C) for several hours to several ten hours.

[0066]

In the case of synthesizing the polymer (B) by radical polymerization in the present invention, a chain transfer agent may be added for the purpose of controlling the molecular weight. Examples of the chain transfer agent include alkyl mercaptans such as n-dodecyl mercaptan, t-dodecyl mercaptan and n-butyl mercaptan; α-methylstyrene dimer; and the like.

[0067]

The polymer (B) may be polymerized in the absence of the components of the curable composition of the present invention

other than the polymer (B), or may be polymerized in the absence thereof. In the case of performing polymerization in the presence of the components of the curable composition other than the polymer (B), it is preferable to perform polymerization in the presence of the oxyalkylene polymer (A) having a reactive silicon group. When the polymer (B) is polymerized in the presence of the oxyalkylene polymer (A) having a reactive silicon group, the step of mixing can be omitted, and the dispersibility of the polymer (B) in the oxyalkylene polymer (A) having a reactive silicon group can be enhanced. Furthermore, it can be envisaged that a portion of the unsaturated group-containing monomer for the polymer (B) is graft polymerized to the oxyalkylene polymer (A) having a reactive silicon group during the polymerization, and in this case, the graft polymerization product functions as a compatibilizer, thereby the dispersibility of the polymer (B) being further enhanced.

[0068]

According to the present invention, the polymer (B) is preferably a polymer containing the aforementioned (meth)acrylic acid alkyl ester monomer unit and having a reactive silicon group represented by the following formula (1):

$$-SiX_aR^1_{(3-a)} \qquad (1)$$

wherein R^1, X and a have the same meanings as previously defined for R^1, X and a.

[0069]

When the polymer (B) has the reactive silicon group represented by the formula (1), the number and the site of presence of the reactive silicon group in the molecule of the polymer (B) are not particularly limited. The number of the reactive silicon group of 1 or greater is acceptable, and the site of presence may be at the termini of the molecule or in a side chain, or the site of presence may also be at both the termini and the side chain.

[0070]

As the method of introducing the reactive silicon group represented by the formula (1) into the polymer (B), the following methods (i) to (iv) may be mentioned. Additionally, the following methods (i) to (iv) may also be carried out in combination.

(i) A method of performing polymerization using an unsaturated group-containing monomer having the reactive silicon group represented by the formula (1) as a part of the unsaturated group-containing monomer according to the present invention.

(ii) A method of polymerizing the unsaturated group-containing monomer according to the present invention, using a chain transfer agent having the reactive silicon group represented by the formula (1).

(iii) A method of polymerizing the unsaturated group-containing monomer according to the present invention, using an initiator having the reactive silicon group represented by the formula (1).

(iv) A method of performing polymerization using an unsaturated group-containing monomer having a functional group such as a hydroxyl group, an amino group, a carboxyl group, an isocyanate group or an epoxy group as a part of the unsaturated group-containing monomer according to the present invention, and reacting the resultant product with a compound having the reactive silicon group represented by the formula (1) and a functional group capable of reacting with the foregoing functional group.

[0071]

As the unsaturated group-containing monomer having the reactive silicon group represented by the formula (1), which may be used in the method (i), a compound represented by the following formula (14) is preferred:

$$R^7\text{-}SiX_aR^1{}_{(3-a)} \qquad (14)$$

wherein R^7 represents a monovalent organic group having an unsaturated group; and R^1, X and a have the same meanings as previously defined for R^1, X and a.

[0072]

Examples of the compound represented by the formula (14) include vinylsilanes such as vinylmethyldimethoxysilane, vinylmethyldiethoxysilane, vinylmethyldichlorosilane, vinyltrimethoxysilane, vinyltriethoxysilane, vinyltrichlorosilane and tris(2-methoxyethoxy)vinylsilane; (meth)acryloyloxysilanes such as 3-acryloyloxypropylmethyldimethoxysilane, 3-methacryloyloxypropylmethyldimethoxysilane,

3-acryloyloxypropyltrimethoxysilane,
3-acryloyloxypropyltriethoxysilane,
3-methacryloyloxypropyltrimethoxysilane and
3-methacryloyloxypropyltriethoxysilane; and the like. Among the above compounds, 3-acryloyloxypropyltrimethoxysilane and 3-methacryloyloxypropyltrimethoxysilane are particularly preferred. These monomers can be used singly or in combination of two or more kinds.

[0073]

The unsaturated group-containing monomer having the reactive silicon group represented by the formula (1) is preferably contained in an amount of 0.01 to 20% by mass in 100 parts by mass of all of the monomers used in the synthesis of the polymer (B).

[0074]

The chain transfer agent having the reactive silicon group represented by the formula (1), which may be used in the method (ii), is preferably a compound represented by the following formula (15), or a compound represented by the following formula (16):

$$HS\text{-}R^8\text{-}SiX_aR^1_{(3-a)} \qquad (15)$$

wherein R^8 represents a single bond or a divalent organic group; and R^1, X and a have the same meanings as previously defined for R^1, X and a.

[Chemical Formula 1]

wherein R^1, R^8, X and a have the same meanings as previously

defined for R^1, R^8, X and a.

[0075]

Examples of the compound represented by the formula (15) include mercaptan compounds having a hydrolyzable silyl group, such as γ-mercaptopropyltrimethoxysilane, γ-mercaptopropylmethyldimethoxysilane, γ-mercaptopropyltriethoxysilane, γ-mercaptopropylmethyldiethoxysilane, and γ-mercaptopropyltriisopropenyloxysilane; and the like. Examples of the compound represented by the formula (16) include $(CH_3O)_3Si\text{-}S\text{-}S\text{-}Si(OCH_3)_3$, $(CH_3O)_3Si\text{-}(CH_2)_3\text{-}S\text{-}S\text{-}(CH_2)_3\text{-}Si(OCH_3)_3$ and the like.

[0076]

In the method (iii), for example, an azo compound having the reactive silicon group represented by the formula (1) can be used as an initiator, and in the method (iv), for example, a polymer (B) having an isocyanate group can be reacted with the compound represented by the formula (10).

[0077]

The molecular weight of the polymer (B) explained above is not particularly limited, but the Mn is preferably 500 to 100000, and more preferably 2000 to 13000. If the Mn of the polymer (B) exceeds 100000, workability tends to undergo a decrease. If the Mn is less than 500, the weather resistance tends to be unsatisfactory.

[0078]

When the polymer (B) has the reactive silicon group

represented by the formula (1), bonds are generated between the reactive silicon groups in the polyoxyalkylene polymer (A) during curing. Thus, when the polymer (B) having the reactive silicon group is used, the strength, weather resistance or the like of the curable composition after curing can be enhanced. Furthermore, a polymer (B) having reactive silicon groups at the molecular termini can be obtained by the method (ii) of using a chain transfer agent having the reactive silicon group, or the method (iii) of using an initiator having the reactive silicon group. Thus, by using such a polymer (B), it is possible to enhance, in particular, the elongation properties of the curable composition after curing.

[0079]

Next, the macromolecular plasticizer (C) having an average molecular weight of 1000 or more according to the present invention will be explained. As the plasticizer that is added to polymeric materials, generally phthalic acid esters such as dimethyl phthalate and dioctyl phthalate; aliphatic dibasic acid esters such as di-2-ethylhexyl adipate and dibutyl sebacate; phosphoric acid esters such as tributyl phosphate and triphenyl phosphate; and the like are used, and these plasticizers are all low molecular weight plasticizers having a molecular weight of 500 or less. In this regard, a compound generally known as a macromolecular plasticizer and having an average molecular weight of 1000 or more, is used in the present invention.

[0080]

The average molecular weight of the macromolecular plasticizer according to the present invention refers to the Mn measured by GPC using a tetrahydrofuran solvent and calculated relative to styrene standards. However, for the average molecular weight of a macromolecular plasticizer having hydroxyl groups at the molecular termini, the molecular weight is not determined by GPC, but the molecular weight calculated in terms of the hydroxyl group value is used. Furthermore, even if the terminal groups in the molecule are not hydroxyl groups, in the case of a macromolecular plasticizer that is likely to be obtained by modifying a terminal hydroxyl group with a low molecular weight compound, the molecular weight calculated in terms of the hydroxyl group value is measured before such modification with a low molecular weight compound, and that value is used to calculate the molecular weight after the modification. Here, the molecular weight calculated in terms of the hydroxyl group value refers to the molecular weight determined by calculation from the mole number of hydroxyl group in one polymer molecule, which is derived from the hydroxyl group value, and the number of active hydrogen atoms of the initiator used in the production of the polymer.

[0081]

Examples of the macromolecular plasticizer (C) having an average molecular weight of 1000 or more that is used in the present invention, include an oxyalkylene polymer, a polyester, poly-α-methylstyrene, polystyrene, polybutadiene, an alkyd resin, polychloroprene, polyisoprene, polybutene,

hydrogenated polybutene, epoxidated polybutadiene, a butadiene-acrylonitrile copolymer, and the like, as well as mixtures thereof.

[0082]

It is preferable that at least a part of the macromolecular plasticizer (C) be an oxyalkylene polymer which does not have a reactive silicon group represented by the following formula (1) (hereinafter, referred to as a reactive silicon group-non-containing oxyalkylene polymer):

$$-SiX_aR^1_{(3-a)} \qquad (1)$$

wherein R^1, X and a have the same meaning as previously defined for R^1, X and a.

[0083]

That is, the macromolecular plasticizer (C) according to the present invention is preferably a mixture of the reactive silicon group-non-containing oxyalkylene polymer and another macromolecular plasticizer, and more preferably only the reactive silicon group-non-containing oxyalkylene polymer. In both of these cases, the reactive silicon group-non-containing oxyalkylene polymer can be used singly or in combination of two or more kinds.

[0084]

The reactive silicon group-non-containing oxyalkylene polymer is desirably a polymer having oxyalkylene as a repeating unit, and the oxyalkylene may be composed of only one kind, or may be composed of two or more kinds. Particularly, when the repeating units are composed of two or more kinds of

oxyalkylenes, the respective oxyalkylenes may be randomly linked to form a random polymer of oxyalkylenes, or oxyalkylenes of same kinds may be linked in a block shape to form a block copolymer. Furthermore, the reactive silicon group-non-containing oxyalkylene polymer may also have, as a repeating unit, a chemical structure other than oxyalkylene in the molecule. Furthermore, it is preferable for the reactive silicon group-non-containing oxyalkylene to have a functional group other than the reactive silicon group represented by the formula (1), or a hydroxyl group, at the termini and/or side chain of the polymer.

[0085]

By subjecting a cyclic ether such as ethylene oxide, propylene oxide, 1,2-butylene oxide, 2,3-butylene oxide or tetrahydrofuran (preferably, propylene oxide) to ring-opening polymerization using an active hydrogen-containing compound such as a monohydric or polyhydric alcohol or a monovalent or polyvalent carboxylic acid as an initiator, and using an alkali metal catalyst such as a potassium-based compound or a cesium-based compound, a composite metal cyanide complex catalyst, a metal porphyrin catalyst or the like as a polymerization catalyst, a hydroxyl group-terminated oxyalkylene polymer can be obtained. This hydroxyl group-terminated oxyalkylene polymer can be used as the reactive silicon group-non-containing oxyalkylene polymer according to the present invention.

[0086]

The hydroxyl group-terminated oxyalkylene polymer obtained by the method described above can be further multimerized by means of a polyhalogen compound, and can acquire a higher molecular weight by means of polyisocyanate, polycarboxylic acid, polycarboxylic acid halide or the like. The polymer thus obtained can also be used as the reactive silicon group-non-containing oxyalkylene polymer according to the present invention.

[0087]

When the hydroxyl group-terminated oxyalkylene polymer is reacted with a compound having a group capable of reacting with a hydroxyl group and a group other than the reactive silicon group represented by the formula (1) (hereinafter, referred to as compound 2), an oxyalkylene polymer in which the hydroxyl group has been converted to a group other than the reactive silicon group, can be obtained. This polymer can also be used as the reactive silicon group-non-containing oxyalkylene polymer according to the present invention.

[0088]

In the case of using, for example, a halogen atom, a carboxyl group (or a haloformyl group) or an isocyanate group as the group capable of reacting with a hydroxyl group in the compound 2, the group other than the reactive silicon group represented by the formula (1) is introduced into the oxyalkylene polymer via an ether bond, an ester bond or a urethane bond, respectively. Examples of the group other than the reactive silicon group represented by the formula (1) that

is introduced into the oxyalkylene polymer, include an unsaturated group such as a vinyl group, a (meth)acryloyl group or a group represented by the following formula (3) (preferably, an allyl group), and an alkyl group:

$$-R^2-CH=CH_2 \qquad (3)$$

wherein R^2 represents a divalent hydrocarbon group having 1 to 18 carbon atoms.

[0089]

According to the present invention, an oxyalkylene polymer resulting from dimerization of an oxyalkylene polymer in which the number of terminal hydroxyl groups in the hydroxyl group-terminated oxyalkylene polymer is 1, through a diether bond, a diester bond, a dicarbanate bond or the like, can also be used as the reactive silicon group-non-containing oxyalkylene polymer.

[0090]

The reactive silicon group-non-containing oxyalkylene polymer according to the present invention preferably has a skeleton formed from an oxyethylene polymer, an oxypropylene polymer, an oxypropylene-oxyethylene copolymer, an oxytetramethylene polymer or an oxytetramethylene-oxyethylene copolymer. As the skeleton of the reactive silicon group-non-containing oxyalkylene polymer, an oxypropylene polymer is particularly preferred.

[0091]

According to the present invention, when the macromolecular plasticizer (C) having average molecular weight

of 1000 or more is added to the oxyalkylene polymer (A) having a reactive silicon group, which has been modified with the polymer (B), it is possible to obtain weather resistance over a long time, which is impossible in conventional compositions. Furthermore, conventionally known effects such as a decrease in the contaminability of the cured product surfaces, an enhancement of the dryability of a coating material (particularly, an alkyd coating material) in the case of coating a coating material on the surface of the cured product, and a decrease in the contaminability of the coating surface after drying of the coating material, can also be obtained at the same time.

[0092]

The average molecular weight of the macromolecular plasticizer (C) according to the present invention is preferably 1000 to 50000, and more preferably 1000 to 20000. When the average molecular weight of the macromolecular plasticizer is less than 1000, the effect of enhancing weather resistance over a long time cannot be obtained. When the average molecular weight exceeds 50000, the workability in the case of using the obtained curable composition as a sealant, an elastic adhesive or the like, tends to undergo a decrease.

[0093]

Furthermore, the viscosity of the macromolecular plasticizer (C) according to the present invention is preferably 5 Pa·s or less at 25°C. The lower limit of the viscosity is not particularly limited, but is preferably 0.1

Pa·s or more. When the viscosity of the macromolecular plasticizer (C) exceeds 5 Pa·s, the resulting curable composition tends to have poor workability.

[0094]

Particularly, when the macromolecular plasticizer (C) is a reactive silicon group-non-containing oxyalkylene polymer, the molecular weight distribution (Mw/Mn) of the polymer is preferably 1.0 to 1.7. The ratio Mw/Mn of the reactive silicon group-non-containing oxyalkylene polymer is more preferably 1.0 to 1.6, and even more preferably 1.0 to 1.5. When the ratio Mw/Mn of the reactive silicon group-non-containing oxyalkylene polymer is as narrow as 1.0 to 1.7, the resulting composition is characterized in that even though the composition has a relatively low viscosity, the composition has less low molecular weight components. Therefore, a cured product having satisfactory weather resistance can be obtained without highly increasing the viscosity of the composition. Furthermore, a cured product having a high effect of improving the adhesiveness of coating material or a high effect of reducing the contaminability of a coating surface, can be obtained. A reactive silicon group-non-containing oxyalkylene polymer having a ratio Mw/Mn of 1.0 to 1.7 can be synthesized by, for example, using the composite metal cyanide complex mentioned above as a catalyst.

[0095]

The curable composition of the present invention contains the oxyalkylene polymer (A), polymer (B) and macromolecular

plasticizer (C) explained above. The composition ratio of these components is not particularly limited, but according to the present invention, the content of the polymer (B) is preferably 1 to 30000 parts by mass, more preferably 1 to 10000 parts by mass, and particularly preferably 1 to 1000 parts by mass, relative to 100 parts by mass of the oxyalkylene polymer (A). Furthermore, the content of the macromolecular plasticizer (C) is preferably 1 to 200 parts by mass, more preferably 5 to 100 parts by mass, and particularly preferably 10 to 70 parts by mass, relative to 100 parts by mass of the sum of the oxyalkylene polymer (A) and the polymer (B).

[0096]

According to the present invention, it is preferable to use an oxyalkylene polymer (A) having a viscosity at 25°C of 20 Pa·s or less and a macromolecular plasticizer (C) having a viscosity at 25°C of 5 Pa·s or less in combination. When such a combination is adopted, in the case of using the resulting curable composition as, for example, a sealant or an elastic adhesive, workability can be made particularly satisfactory.

[0097]

The curable composition of the present invention can be obtained by, for example, synthesizing the oxyalkylene polymer (A) according to the method described above, subsequently synthesizing the polymer (B) according to the method described above apart from the oxyalkylene polymer (A), and mixing these with the macromolecular plasticizer (C). The curable composition can also be obtained by synthesizing the

oxyalkylene polymer (A), subsequently synthesizing the polymer (B) in the presence of the former polymer, adding the macromolecular plasticizer (C) thereto, and mixing the contents. In the case of the latter, the synthesis of the polymer (B) may be carried out in the presence of both the oxyalkylene polymer (A) and the macromolecular plasticizer (C). Furthermore, an organic solvent can be used upon synthesis or mixing, and after the synthesis or mixing, this organic solvent can be removed according to necessity.

[0098]

The curable composition of the present invention may also contain, in addition to the oxyalkylene polymer (A), polymer (B) and macromolecular plasticizer (C), additive components such as a filler, a curing accelerator, an adhesiveness imparting agent, a dehydrating agent, an age resister, a thixotropic agent, a solvent, and a low molecular weight plasticizer. The method of adjusting the curable composition containing these additive components is not particularly limited, and the additive components may be added all in one time or in several divided portions, at an appropriate timing in the middle of the production or after the production of the curable composition. These additive components will be explained below.

[0099]

First, the filler that can be used in the curable composition of the present invention will be explained. According to the present invention, filler can be added to the

curable composition. Examples of the filler include calcium carbonates such as heavy calcium carbonate having an average particle size of 1 to 20 μm, light calcium carbonate having an average particle size of 1 to 3 μm produced by a precipitation method, colloidal calcium carbonate which has been surface treated with fatty acids or a resin acid-based organic substance, and ultrafine calcium carbonate; fumed silica; precipitated silica; surface silicon-treated silica fine powder; silicic anhydride; hydrated silicic acid; carbon black; magnesium carbonate; diatomaceous earth; calcined clay; clay; talc; titanium oxide; bentonite; ferric oxide; zinc oxide; activated zinc oxide; inorganic hollow bodies such as Shirasu balloon, pearlite, glass balloon, silica balloon, fly ash balloon, alumina balloon, zirconia balloon, and carbon balloon; organic resin hollow bodies such as phenolic resin balloon, epoxy resin balloon, urea resin balloon, saran balloon, polystyrene balloon, polymethacrylate balloon, polyvinyl alcohol balloon, styrene-acrylic resin balloon, and polyacrylonitrile balloon; powder-form fillers such as resin beads, wood flour, pulp, cotton chips, mica, walnut shell powder, rice husk powder, graphite, aluminum fine powder, and flint powder; and fibrous fillers such as glass fiber, glass filament, carbon fiber, kevlar fiber, and polyethylene fiber.

[0100]

These fillers may be used singly, or may be used in combination of two or more kinds. Among these, it is preferable to use calcium carbonate, and it is particularly preferable to

use heavy calcium carbonate and colloidal calcium carbonate in combination. If hollow bodies are used, the curable composition and a cured product thereof can be made lightweight. Furthermore, use of hollow bodies can improve the threading properties of the composition, thereby enhancing workability. The hollow bodies may be used singly, but the hollow bodies may also be used in combination with other fillers such as calcium carbonate.

[0101]

The amount of use of the filler according to the present invention is preferably 1 to 1000 parts by mass, and more preferably 50 to 250 parts by mass, relative to 100 parts by mass of the sum of the oxyalkylene polymer (A) and the polymer (B).

[0102]

Next, the curing accelerator that can be used in the curable composition of the present invention will be explained. Although the crosslinking reaction of the reactive silicon group contained in the oxyalkylene polymer (A) according to the present invention proceeds even in the absence of a compound that accelerates the reaction, if the reactive silicon group is, for example, an alkoxysilyl group, it is preferable to use a curing accelerator in order to manifest a practically sufficient curing rate.

[0103]

Examples of the curing accelerator include a divalent tin compound such as tin 2-ethylhexanoate, tin naphthenate or tin

stearate; organotin carboxylates, including a dialkyltin dicarboxylate such as dibutyltin dilaurate, dibutyltin diacetate, dibutyltin monoacetate or dibutyltin maleate, or a dialkoxytin monocarboxylate; a tin chelating compound such as dialkyltin bisacetylacetonate or dialkyltin monoacetylacetonate monoalkoxide; a reaction product of a dialkyltin oxide and an ester compound; a reaction product of a dialkyltin oxide and an alkoxysilane compound; and a tetravalent tin compound such as dialkyltin dialkylsulfide.

[0104]

Examples of the tin chelating compound include dibutyltin bisacetylacetonate, dibutyltin bisethylacetoacetate, dibutyltin monoacetylacetonate monoalkoxide, and the like. The reaction product of a dialkyltin oxide and an ester compound may be a tin compound which is prepared by mixing and heating dibutyltin oxide and a phthalic acid ester such as dioctyl phthalate or diisononyl phthalate to react, and converted into a liquid. In this case, as the ester compound, aliphatic or aromatic carboxylic acid esters other than phthalic acid esters, tetraethyl silicate or partially hydrolyzed condensates thereof, and the like can also be used. Compounds prepared by reacting or mixing these tin compounds with low molecular weight alkoxysilanes or the like, can also be preferably used.

[0105]

Examples of the curing catalyst that can be used in addition to the tin compounds, include a divalent bismuth compound such as an organic carboxylic acid bismuth salt; an

acidic compound such as phosphoric acid, p-toluenesulfonic acid, phthalic acid or di-2-ethylhexyl phosphate; and amine compounds, including an aliphatic monoamine such as butylamine, hexylamine, octylamine, decylamine, laurylamine or N,N-dimethyloctylamine; an aliphatic polyamine compound such as ethylenediamine, hexamethylenediamine, diethylenetriamine, triethylenetetramine or tetraethylenepentamine; an aromatic amine compound; an alkanolamine; and an aminosilane coupling agent such as N-(2-aminoethyl)-3-aminopropyltrimethoxysilane or 3-aminopropyltrimethoxysilane. Since the divalent tin compound or the divalent bismuth compound enhances the curing accelerating effect when used in combination with a primary amine compound, it is preferable to use the compounds in combination.

[0106]

The curing accelerators mentioned above can be used singly or in combination of two or more kinds. The amount of addition of the curing accelerator in the case of using a curing accelerator, is preferably set at 0.1 to 10 parts by mass relative to 100 parts by mass of the sum of the oxyalkylene polymer (A) and the polymer (B).

[0107]

Next, the adhesiveness imparting agent that can be used in the curable composition of the present invention will be explained. According to the present invention, an adhesiveness imparting agent may be added to the curable composition for the purpose of improving adhesiveness.

Examples of the adhesiveness imparting agent include silane coupling agents such as a (meth)acryloyloxy group-containing silane, an amino group-containing silane, a mercapto group-containing silane, an epoxy group-containing silane and a carboxyl group-containing silane.

[0108]

Examples of the (meth)acryloyloxy group-containing silane include 3-methacryloyloxypropyltrimethoxysilane, 3-acryloyloxypropyltrimethoxysilane, 3-methacryloyloxypropylmethyldimethoxysilane, and the like. Examples of the amino group-containing silane include 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 3-aminopropylmethyldimethoxysilane, N-(2-aminoethyl)-3-aminiopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane, N-(2-aminoethyl)-3-aminopropyltriethoxysilane, 3-ureidopropyltriethoxysilane, N-(N-vinylbenzyl-2-aminoethyl)-3-aminopropyltrimethoxysilane, 3-anilinopropyltrimethoxysilane, and the like.

[0109]

Examples of the mercapto group-containing silane include 3-mercaptopropyltrimethoxysilane, 3-mercaptopropyltriethoxysilane, 3-mercaptopropylmethyldimethoxysilane, 3-mercaptopropylmethyldiethoxysilane, and the like. Examples of the epoxy group-containing silane include 3-glycidyloxypropyltrimethoxysilane,

3-glycidyloxypropylmethyldimethoxysilane, 3-glycidyloxypropyltriethoxysilane, and the like. Examples of the carboxyl group-containing silane include 2-carboxyethyltriethoxysilane, 2-carboxyethylphenylbis(2-methoxyethoxy)silane, N-(N-carboxylmethyl-2-aminoethyl)-3-aminopropyltrimethoxysilane, and the like.

[0110]

Furthermore, a reaction product obtainable by reacting two or more silane coupling agents may also be used. Examples of such a reaction product include a reaction product of an amino group-containing silane and an epoxy group-containing silane, a reaction product of an amino group-containing silane and a (meth)acryloyloxy group-containing silane, a reaction product of an epoxy group-containing silane and a mercapto group-containing silane, a reaction product of mercapto group-containing silanes, and the like. These reaction products can be easily obtained by mixing silane coupling agents and stirring the mixture at a temperature in the range of room temperature to 150°C for 1 to 8 hours.

[0111]

The above compounds may be used singly, or may be used in combination of two or more kinds. The amount of use of the silane coupling agent is preferably 0 to 30 parts by mass relative to 100 parts by mass of the sum of the oxyalkylene polymer (A) and the polymer (B).

[0112]

According to the present invention, an epoxy resin can also be added as the adhesiveness imparting agent. Examples of the epoxy resin that can be added to the curable composition of the present invention, include epoxy resins, including flame retardant type epoxy resins such as bisphenol A-diglycidyl ether type epoxy resins, bisphenol F-diglycidyl ether type epoxy resins, and tetrabromobisphenol A-glycidyl ether type epoxy resins; novolac type epoxy resins; hydrogenated bisphenol A type epoxy resins; glycidyl ether type epoxy resins of bisphenol A/propylene oxide adducts; diglycidyl ester-based epoxy resins such as glycidyl 4-glycidyloxybenzoate, diglycidyl phthalate, diglycidyl tetrahydrophthalate, and diglycidyl hexahydrophthalate; m-aminophenol-based epoxy resins; diaminodiphenylmethane-based epoxy resins; urethane-modified epoxy resins; various alicyclic epoxy resins; glycidyl ethers of polyhydric alcohols, such as N,N-diglycidylaniline, N,N-diglycidyl-o-toluidine, triglycidyl isocyanurate, polyalkylene glycol diglycidyl ether and glycerin; hydantoin type epoxy resins; epoxides of unsaturated polymers such as petroleum resins; vinyl polymers containing epoxy groups, and the like. The amount of use in the case of adding an epoxy resin is preferably 0 to 100 parts by mass relative to 100 parts by mass of the oxyalkylene polymer (A).

[0113]

In the case of adding an epoxy resin such as mentioned above to the curable composition of the present invention, a

curing agent (or curing catalyst) for the epoxy resin may be further added. Examples of such a curing agent include amines or salts thereof, such as triethylenetetramine, tetraethylenepentamine, diethylaminopropylamine, N-aminoethylpiperazine, m-xylenediamine, m-phenylenediamine, diaminodiphenylmethane, diaminodiphenylsulfone, isophorone diamine and 2,4,6-tris(dimethylaminomethyl)phenol, or blocked amines of ketimine compounds or the like; polyamide resins; imidazole compounds; dicyandiamide; boron trifluoride complex compounds; carboxylic acid anhydrides such as phthalic anhydride, hexahydrophthalic anhydride, tetrahydrophthalic anhydride, dodecenylsuccinic acid anhydride and pyromellitic acid anhydride; phenoxy resins; carboxylic acids; alcohols; oxyalkylene-based polymers having, on an average, at least one group capable of reacting with an epoxy group in the molecule (terminal aminated polyoxypropylene glycol, terminal carboxylated polyoxypropylene glycol, and the like); liquid terminal functional group-containing polymers such as polybutadiene, hydrogenated polybutadiene, an acrylonitrile-butadiene copolymer or an acrylic polymer, each having the termini modified with a hydroxyl group, a carboxyl group, an amino group or the like; ketimine compounds, and the like. The amount of use in the case of using an epoxy resin curing agent is preferably 0.1 to 300 parts by mass based on the epoxy resin.

[0114]

Next, the dehydrating agent that can be used in the curable

composition of the present invention will be explained. According to the present invention, a small amount of a dehydrating agent can be added to an extent that there is no adverse effect on curability or flexibility, in order to improve the storage stability of the curable composition. Examples of such a dehydrating agent include alkyl orthoformates such as methyl orthoformate and ethyl orthoformate; alkyl orthoacetates such as methyl orthoacetate and ethyl orthoacetate; hydrolyzable organosilicon compounds such as methyltrimethoxysilane, vinyltrimethoxysilane, tetramethoxysilane and tetraethoxysilane; hydrolyzable organotitanium compounds; and the like. Among them, vinyltrimethoxysilane and tetraethoxysilane are particularly preferred from the viewpoints of price and effects. For a one-liquid blend which is prepared by adding a curing catalyst or the like to the curable composition of the present invention and is used while filled in a moisture-proof container, such a dehydrating agent is particularly effective. The amount of use of the dehydrating agent in the present invention is preferably set at 0.1 to 30 parts by mass relative to 100 parts by mass of the sum of the oxyalkylene polymer (A) and the polymer (B).

[0115]

Next, the age resister that can be used in the curable composition of the present invention will be explained. According to the present invention, an age resist can be added to the curable composition. Examples of the age resister

include an antioxidant, an ultraviolet absorbent, a photostabilizer and the like, and hindered amine-based compounds, benzotriazole-based compounds, benzophenone-based compounds, benzoate-based compounds, cyanoacrylate-based compounds, acrylate-based compounds, hindered phenol-based compounds, phosphorus-based compounds, and sulfur-based compounds can be used. In particular, it is preferable to use two or more of a photostabilizer, an antioxidant and an ultraviolet absorbent in combination. Such a method of use allows the characteristics of each of the components to be manifested and thus can enhance the age resisting effect. Specifically, it is particularly effective to use a combination of two or more kinds selected from tertiary and secondary hindered amine-based photostabilizers, benzotriazole-based ultraviolet absorbents, hindered phenol-based and phosphite-based antioxidants. The amounts of use of the antioxidant, ultraviolet absorbent and photostabilizer are preferably 0.1 to 10 parts by mass, respectively, relative to 100 parts by mass of the sum of the polyoxyalkylene polymer (A) and the polymer (B). If the amount of use is less than 0.1 parts by mass, the age resisting effect is not manifested sufficiently, and if the amount of use exceeds 10 parts by mass, it is economically disadvantageous.

[0116]

Next, the thixotropic agent that can be used in the curable composition of the present invention will be explained. According to the present invention, a thixotropic agent can be

added to the curable composition. Addition of the thixotropic agent improves the sagging properties of the curable composition. Examples of the thixotropic agent include hydrogenated castor oil, fatty acid amides, calcium stearate, zinc stearate, finely powdered silica, organic acid-treated calcium carbonate, and the like. It is preferable to add the thixotropic agent in an amount of 0.5 to 10 parts by mass relative to 100 parts by mass of the sum of the oxyalkylene polymer (A) and the polymer (B).

[0117]

Next, the solvent that can be used in curable composition of the present invention will be explained. According to the present invention, a solvent can be added to the curable composition for the purpose of adjusting viscosity and enhancing the storage stability of the composition. Examples of such a solvent include aliphatic hydrocarbons, aromatic hydrocarbons, halogenated hydrocarbons, alcohols, ketones, esters, ethers and the like. When an alcohol is added, the storage stability of the curable composition of the present invention is enhanced. Therefore, in the case of storing the curable composition for a long time, it is preferable to add an alcohol. Examples of such an alcohol include alkyl alcohols having 1 to 10 carbon atoms, such as methanol, ethanol, isopropyl alcohol, isopentyl alcohol and hexyl alcohol. It is preferable to add the solvent in an amount of 0.1 to 500 parts by mass relative to 100 parts by mass of the sum of the oxyalkylene polymer (A) and the polymer (B).

[0118]

Next, the low molecular weight plasticizer that can be used in the curable composition of the present invention will be explained. According to the present invention, a low molecular weight plasticizer can be added to the curable composition. Examples of the low molecular weight plasticizer include phthalic acid esters such as di(2-ethylhexyl) phthalate, dimethyl phthalate, dibutyl phthalate, butyl benzyl phthalate and diisononyl phthalate; aliphatic dibasic acid esters such as dioctyl adipate, di-2-ethylhexyl adipate, dibutyl sebacate, bis(2-methylnonyl) succinate, and butyl oleate; phosphoric acid ester such as tributyl phosphate, triphenyl phosphate, trioctyl phosphate and tricresyl phosphate; epoxy compounds such as di(2-ethylhexyl) 4,5-epoxycyclohexane-1,2-dicarboxylate and benzyl epoxystearate; and the like.

[0119]

The above low molecular weight plasticizers may be used singly or may be used in combination of two or more kinds. If the amount of addition of the low molecular weight plasticizer is large, the high weather resistance of the curable composition of the present invention may be impaired. Thus, it is preferable to add the low molecular weight plasticizer in an amount of 100 parts by mass or less, and more preferably 50 parts by mass or less, relative to 100 parts by mass of the macromolecular plasticizer (C).

[0120]

Next, additive components other than those mentioned above, which can be used in the curable composition of the present invention, will be explained. According to the present invention, it is possible to add an air oxidation-curable compound or a photocurable compound to the curable composition. By adding these compounds, weather resistance or attachment of sand dust is improved. These compounds may be used singly, but it is more preferable to use them in combination. In the case of adding the air oxidation-curable compound, the amount of use is preferably 0.1 to 50 parts by mass relative to 100 parts by mass of the sum of the oxyalkylene polymer (A) and the polymer (B), and in the case of adding the photocurable compound, the amount of use is preferably 0.1 to 50 parts by mass relative to 100 parts by mass of the sum of the oxyalkylene polymer (A) and the polymer (B).

[0121]

Examples of the air oxidation-curable compound include drying oils such as wood oil or linseed oil; alkyd resins obtainable by modifying drying oils; acrylic polymers modified with drying oils; silicone resins; diene-based polymers such as polybutadiene, and polymers or copolymers of a diene having 5 to 8 carbon atoms; modification products (maleation modification, boiled oil modification or the like) of these polymers or copolymers; air-curable polyester compounds, and the like.

[0122]

Examples of the photocurable compound include

polyfunctional (meth)acrylates, and examples of the polyfunctional (meth)acrylates include (meth)acrylic acid esters of polyhydric alcohols, such as tetraethylene glycol diacrylate, pentaerythritol triacrylate and trimethylolpropane triacrylate. Here, this photocurable compound is a monomer, and is distinguished from the polymer (B) formed from unsaturated group-containing monomers including the (meth)acrylic acid alkyl ester monomer.

[0123]

According to the present invention, a compound which generates trimethylsilanol by hydrolysis may be added to the curable composition as a modulus adjusting agent. When such a compound is added, the modulus of the cured product obtainable particularly in the case of using a divalent tin compound and a primary amine compound as curing accelerating agents, is decreased, and the surface stickiness is also reduced. As the compound generating trimethylsilanol, trimethylsilyl ethers of an aliphatic alcohol, phenol and the like can be used. As the acidity of the alcohol is stronger, the compound has an effect of further delaying curing. It is also possible to adjust curability by arbitrarily changing the type of alcohol, and for that purpose, trimethylsilyl ethers of a plurality of alcohols can be used at the same time. Hexamethyldisilazane can also be used. The amount of use in the case of using a compound generating trimethylsilanol is preferably 0.1 to 10 parts by mass relative to 100 parts by mass of the sum of the oxyalkylene polymer (A) and the polymer (B).

[0124]

In addition to the compounds mentioned above, inorganic pigments such as iron oxide, chromium oxide and titanium oxide; and organic pigments such as Phthalocyanine Blue and Phthalocyanine Green can be added to the curable composition. When pigments are added, the curable composition is colored, but additionally, effects such as an enhancement of weather resistance can be expected.

[0125]

Furthermore, particularly for the purpose of imparting designability as a sealant, it is possible to allow the curable composition to have a surface appearance such as that of granite, by adding microbodies having a color different from the color of the composition to the curable composition. Furthermore, it is also possible to add a flame retardant, an antifungal agent, a matting agent which is in use for coating applications, and the like.

[0126]

As discussed above, the curable composition of the present invention contains, as essential components, (A) the oxyalkylene polymer having a reactive silicon group, (B) the polymer containing a (meth)acrylic acid alkyl ester monomer unit, and (C) the macromolecular plasticizer having an average molecular weight of 1000 or more. In the curable composition of the present invention, the macromolecular plasticizer (C) having an average molecular weight of 1000 or more exhibits an effect of enhancing weather resistance over a long time, in a

combination with the oxyalkylene polymer (A) modified with the polymer (B). Therefore, the curable composition of the present invention can be used as a sealant, a waterproof material, an adhesive, a coating agent or the like, and in particular, the curable composition can be suitably used in the applications that are prone to be exposed to wind and rain, sunlight or the like for a long time in the outdoor.

[0127]

When used in such applications, the curable composition of the present invention can be formulated into a one-liquid blend or a two-liquid blend. The one-liquid blend is a single-component type blend containing a curable oxyalkylene polymer and a curing accelerating agent in a same blend, and is a moisture-curable type blend which is stored in a moisture-tight state, and reacts with moisture in air at the time of use, thereby curing from the surface. On the other hand, the two-liquid blend is a two-component type blend including a main agent that contains a curable oxyalkylene polymer as a main component and a curing agent that contains a curing accelerating agent as a main component, and is a reaction-curable type blend which cures when the two agents are mixed at the time of use and thereby react with each other.

[0128]

[Examples]

Hereinafter, suitable Examples of the present invention will be explained in more detail, but the present invention is not intended to be limited to these Examples. In the following

Preparation Examples, Examples and Comparative Examples, the term parts mean parts by mass. Furthermore, the Mn and Mw/Mn were determined by GPC as described above, and the viscosity was determined by a B type viscometer.

[0129]

(Preparation Example 1-1)

To a polyoxypropylene triol having an Mn value of 17000 and an Mw/Mn value of 1.4, which was obtained by reacting propylene oxide using glycerin as an initiator and in the presence of a zinc hexacyanocobaltate-glyme complex catalyst, a methanol solution of sodium methoxide was added, and methanol was distilled off under heat and reduced pressure, to thereby convert the terminal hydroxyl group of the polypropylene oxide into sodium alkoxide. Subsequently, the polypropylene oxide was reacted with allyl chloride, and the polypropylene oxide was subjected to the removal of unreacted allyl chloride and purification. Thus, a polypropylene oxide having allyl groups at the termini was obtained. This reaction product was reacted with methyldimethoxysilane, which is a hydrosilyl compound, in the presence of a platinum catalyst, and thus a polypropylene oxide (P1) having methyldimethoxysilyl groups at the termini was obtained. The viscosity of the obtained polypropylene oxide (P1) at 25°C was 10 Pa·s.

[0130]

(Preparation Example 1-2)

A polyoxypropylene diol having an Mn value of 20000 and an Mw/Mn value of 1.3, which was obtained by reacting propylene

oxide using dipropylene glycol as an initiator and in the presence of a zinc hexacyanocobaltate-glyme complex catalyst, was used to obtain a polypropylene oxide (P2) having methyldimethoxysilyl groups at the termini in the same manner as in the Preparation Example 1-1. The viscosity of the obtained polypropylene oxide (P2) at 25°C was 16 Pa·s.

[0131]

(Preparation Example 1-3)

To a polyoxypropylene polyol prepared by mixing, at a ratio of 84/16 by mass, a polyoxypropylene diol having an Mn value of 3000, which was obtained using propylene glycol as an initiator and a potassium hydroxide catalyst, and a polyoxypropylene triol having an Mn value of 3000, which was obtained using propylene glycol as an initiator and a potassium hydroxide catalyst, sodium hydroxide was added, and the mixture was allowed to react under heating and stirring. Then, the resultant was reacted with bromochloromethane to increase the molecular weight. The number average molecular weight of the obtained polymer was 18000 and the Mw/Mn value was 2.1. Subsequently, the polymer was reacted with allyl chloride, and the polymer was subjected to the removal of volatile substances and purification. Thus, a polypropylene oxide having allyl groups at the termini was obtained. This was reacted with methyldimethoxysilane, which is a hydrosilyl compound, in the presence of a platinum catalyst, and thereby, a polypropylene oxide (P3) having methyldimethoxysilyl groups at the termini was obtained. The viscosity of the resulting polypropylene

oxide (P3) at 25°C was 38 Pa·s.

[0132]

(Preparation Example 2-1)

20 g of the polypropylene oxide (P1) was placed in a reactor equipped with a stirrer, and 40 g of toluene was added thereto to dilute the polymer. This mixture was uniformly mixed while being heated to 100°C. To this mixture, a solution prepared by dissolving 0.4 g of 2,2'-azobisisobutyronitrile in a mixture of 3.3 g of methyl methacrylate, 16.7 g of butyl acrylate, 11.0 g of octadecyl methacrylate, 1.6 g of γ-methacryloxypropyltrimethoxysilane, 6.8 g of styrene and 0.64 g of γ-mercaptopropyltrimethoxysilane, was added dropwise over 3 hours while the mixture was stirred in a nitrogen atmosphere. After completion of the dropwise addition, a toluene solution of 0.3 g of 2,2'-azobisisobutyronitrile was further added dropwise thereto over 30 minutes, and then the resulting mixture was heated and stirred at the same temperature for 3 hours. To the resulting toluene solution of a copolymer, 120 g of the polypropylene oxide (P2) was added, and the mixture was mixed under stirring for 30 minutes. Subsequently, toluene was distilled off at 100°C under reduced pressure, and thus a polymer Pa was obtained.

[0133]

(Preparation Example 2-2)

40 g of xylene was placed in a reactor equipped with a stirrer, and while the temperature was maintained at 110°C, a solution prepared by dissolving 0.4 g of

2,2'-azobisisobutyronitrile in a mixture of 1.5 g of methyl methacrylate, 28.7 g of butyl acrylate, 7.7 g of octadecyl methacrylate, 1.2 g of trimethylolpropane trismethacrylate, 0.19 g of γ-methacryloxypropyltrimethoxysilane and 0.76 g of γ-mercaptopropyltrimethoxysilane, was added dropwise to the reactor over 3 hours, while the mixture was stirred in a nitrogen atmosphere. After completion of the dropwise addition, a toluene solution of 0.3 g of 2,2'-azobisisobutyronitrile was further added dropwise thereto over 30 minutes, and then the resulting mixture was heated and stirred at the same temperature for 3 hours. To the resulting xylene solution of a copolymer, 120 g of the polypropylene oxide (P2) was added, and the mixture was mixed under stirring for 30 minutes. Subsequently, xylene was distilled off at 100°C under reduced pressure, and thus a polymer Pb was obtained.

[0134]

(Preparation Example 2-3)

40 g of xylene was placed in a reactor equipped with a stirrer, and while the temperature was maintained at 110°C, a solution prepared by dissolving 0.4 g of 2,2'-azobisisobutyronitrile in a mixture of 29.2 g of methyl methacrylate, 0.48 g of butyl acrylate, 7.6 g of octadecyl methacrylate, 1.9 g of γ-methacryloxypropyltrimethoxysilane and 0.78 g of γ-mercaptopropyltrimethoxysilane was added dropwise to the above xylene over 3 hours while the mixture was stirred in a nitrogen atmosphere. After completion of the dropwise addition, a toluene solution of 0.3 g of

2,2'-azobisisobutyronitrile was further added dropwise thereto over 30 minutes, and then the resulting mixture was heated and stirred at the same temperature for 3 hours. To the resulting xylene solution of a copolymer, 120 g of the polypropylene oxide (P3) was added, and the mixture was mixed under stirring for 30 minutes. Subsequently, xylene was distilled off at 100°C under reduced pressure, and thus a polymer Pc was obtained.

[0135]

(Preparation Example 3-1)

A polyoxypropylene triol having a molecular weight of 5000 in terms of hydroxyl group value and an Mw/Mn value of 1.3, which was obtained by reacting propylene oxide using glycerin as an initiator and in the presence of a potassium hydroxide catalyst, was used to obtain a polypropylene oxide (K1) having allyl groups at the termini in the same manner as in the Preparation Example 1. The viscosity of the K2 at 25°C was 0.9 Pa·s.

[0136]

(Preparation Example 3-2)

A polyoxypropylene diol having a molecular weight of 3000 in terms of hydroxyl group value and an Mw/Mn value of 1.3 was obtained by performing polymerization of propylene oxide using propylene glycol as an initiator and in the presence of a zinc hexacyanocobaltate-glyme complex catalyst, and then the polyoxypropylene diol was purified (K2). The viscosity of K2 at 25°C was 0.6 Pa·s.

[0137]

(Preparation Example 3-3)

A polyoxypropylene triol having a molecular weight of 10000 in terms of hydroxyl group value and an Mw/Mn value of 1.3, which was obtained by reacting propylene oxide using glycerin as an initiator and in the presence of a zinc hexacyanocobaltate-glyme complex catalyst, was used to obtain a polypropylene oxide (K3) having allyl groups at the termini in the same manner as in the Preparation Example 1. The viscosity of K3 at 25°C was 3 Pa·s.

[0138]

(Preparation Example 3-4)

A polyoxypropylene triol having a molecular weight of 15000 in terms of hydroxyl group value and an Mw/Mn value of 1.3, which was obtained by reacting propylene oxide using glycerin as an initiator and in the presence of a zinc hexacyanocobaltate-glyme complex catalyst, was used to obtain a polypropylene oxide (K4) having allyl groups at the termini in the same manner as in the Preparation Example 1. The viscosity of K4 at 25°C was 9 Pa·s.

[0139]

(Example 1)

To 100 parts by mass of the polymer Pa, a modulus adjusting agent (2-ethylhexyloxytrimethylsilane), an air-curable compound (wood oil) and a thixotropic agent (Disparlon #305) were added in the amounts in parts by mass indicated in Table 1, and the mixture was mixed. Subsequently, a filler (Neolite

SP-T, Whiton SB, or Q-CEL 520), a macromolecular plasticizer (K1), an adhesiveness imparting agent (Epikote 828), a photocurable compound (Aronix M309), and an age resister (Adekastab LA62, Tinuvin 327, or Irganox 1010) were added in the amounts in parts by mass indicated in Table 1 and the mixture was uniformly mixed. These combinations were used as main agents. On the other hand, a curing catalyst (ST/LA) prepared by mixing and reacting 2-ethylhexanetin and laurylamine at a mass ratio of 3:1, a plasticizer (DOP) and a filler (Whiton SB or ASP-170) were mixed in the amounts in parts by mass indicated in Table 1, and these combinations were used as curing agents. Here, the abbreviations used for the raw materials of the curable composition in the Table 1 are marked with the symbol * and numeral references, and the details are indicated in Table 5.

[0140]

(Examples 2 to 7 and Comparative Examples 1 to 2)

The main agents of Examples 2 to 7 and Comparative Examples 1 to 2 were produced with the raw materials and compositions (mass ratio) indicated in Table 1, in the same manner as in the production method for the main agent of Example 1. Furthermore, the curing agents of Examples 2 to 7 and Comparative Examples 1 to 2 were produced in the same manner as in Example 1.

[0141]

[Table 1]

			Example							Comparative Example	
			1	2	3	4	5	6	7	1	2
Main agent	Polymer	Pa	100	-	-	100	-	-	100	-	-
		Pb	-	100	-	-	100	-	-	100	-

		Pc	-	-	100	-	-	100	-	-	-
		P2	-	-	-	-	-	-	-	-	100
	Macromolecular plasticizer	K1	50	50	50	-		-	-	-	50
		K2	-	-	-	50	-	-	-	-	-
		K3	-	-	-	-	30	-	-	-	-
		K4	-	-	-	-	-	50	-	-	-
		K5[*1]	-	-	-	-	-	-	50	-	-
	Low molecular weight plasticizer	DOP[*2]	-	-	-	-	10	-	-	50	-
		Sansocizer[*3]	-	-	-	-	10	-	-	-	-
	Filler	Neolite SP-T[*4]	120	120	120	120	120	120	120	120	120
		Whiton SB[*5]	20	20	20	20	20	20	20	20	20
		Hollow body 1[*6]	3	3	3	-	-	-	3	3	3
		Hollow body 2[*7]	-	-	-	3	-	-	-	-	-
		Hollow body 3[*8]	-	-	-	-	3	-	-	-	-
		Hollow body 4[*9]	-	-	-	-	-	3	-	-	-
	Thixotropic agent	Disparlon #305[*10]	3	3	3	3	3	3	3	3	3
	Modulus adjusting agent	TMP-TMS[*11]	-	-	-	0.7	-	0.4	-	-	-
		2-EHOTMS[*12]	1.3	1.3	1.3	-	-	-	1.3	1.3	1.3
		PhOTMS[*13]	-	-	-	-	-	0.4	-	-	-
		HMDS[*14]	-	-	-	-	0.5	-	-	-	-
	Air-curable compound	Wood oil	3	3	3	-	-	-	3	-	3
	Photocurable compound	Aronix M309[*15]	3	3	3	3	3	3	-	3	3
	Adhesiveness imparting agent	Epikote 828[*16]	5	5	5	5	5	5	5	5	5
	Age resister	Adekastab LA62[*17]	1	1	1	0.5	-	1	1	1	1
		Adekastab LA67[*18]	-	-	-	0.5	1	-	-	-	-
		Tinuvin 327[*19]	1	1	1	1	1	1	1	1	1
		Irganox 1010[*20]	1	1	1	1	1	1	1	1	1
Curing agent	Curing catalyst	ST/LA[*21]	3	3	3	3	3	3	3	3	3
	Plasticizer	DOP[*2]	7	7	7	7	7	7	7	7	7
	Filler	Whiton SB[*5]	20	20	20	20	20	20	20	20	20
		ASP-170[*22]	5	5	5	5	5	5	5	5	5

[0142]

Each of the curable compositions obtained by mixing the main agents and curing agents of Examples 1 to 7 and Comparative Examples 1 to 2, respectively, was applied on a 1 mm-thick aluminum plate to a thickness of 5 mm, and the composition was cured for 7 days at 20°C and at a humidity of 65% to form a cured product having a thickness of 5 mm on the aluminum plate. This was used as a test specimen. This specimen was subjected to a weathering test with a Sunshine Super Long Life Weather Meter

(manufactured by Suga Test Instruments Co., Ltd.), and the surface conditions of the test specimen after 500 hours, after 1000 hours and after 1500 hours were observed. The evaluation was based on the following criteria: ○: no cracks are recognized, △: slight thin cracks are recognized, and ×: obvious cracks are recognized.

[0143]

Subsequently, each of the curable compositions obtained by mixing the main agents and curing agents of Examples 1 to 7 and Comparative Examples 1 to 2, respectively, was applied on a 1 mm-thick aluminum plate to a thickness of 0.2 mm, and the composition was cured for 7 days at 20°C and at a humidity of 65% to form a cured product having a thickness of 0.2 mm on the aluminum plate. This was used as a test specimen. This specimen was subjected to a weathering test with a Sunshine Super Long Life Weather Meter (manufactured by Suga Test Instruments Co., Ltd.), and the surface conditions of the test specimen after 500 hours, after 1000 hours and after 1500 hours were observed. The evaluation was based on the following criteria: ○: whitening is not recognized, △: slight whitening (discoloration) is recognized, and ×: whitening (discoloration) is clearly recognized.

[0144]

In regard to Examples 1 to 7, the workability condition at the time of the mixing operation (manual mixing using a paddle) for the main agent and curing agent, was evaluated based on three grades (workability 1). The evaluation was based on

the following criteria: A: mixable with light force, B: slight force required in the mixing, and C: significant force required in the mixing.

[0145]

The results of the above tests are summarized in the following Table 2. As it is obvious from the results indicated in Table 2, when the thickness was thick (thickness: 5 mm), the cured products of the curable compositions obtained in the Examples 1 to 7 were not recognized to have cracks and exhibited satisfactory weather resistance over a very long time, even at a time point when an exposure time of 1500 hours elapsed. On the other hand, the cured products of the curable compositions obtained in the Comparative Examples 1 to 2 generated cracks at a time point between exposure times of 1000 hours and 1500 hours, for the same thickness.

[0146]

When the thickness was thin (thickness: 0.2 mm), the cured products of the curable compositions obtained in the Examples 1 to 7 were not at all recognized to have whitening at a time point when an exposure time of 1000 hours elapsed, and were recognized to have slight whitening (discoloration) at a time point when an exposure time of 1500 hours elapsed. On the other hand, the cured products of the curable compositions obtained in the Comparative Examples 1 to 2 had whitening occurred at a time point between exposure times of 500 hours and 1000 hours, for the same thickness.

[0147]

It was also shown that all of the curable compositions obtained in the Examples 1 to 7 could be mixed in the manual mixing test using a paddle, and had satisfactory workability.

[0148]

[Table 2]

			Example							Comparative Example	
			1	2	3	4	5	6	7	1	2
Test results	Weather resistance (5 mm thick)	500 hours	○	○	○	○	○	○	○	○	○
		1000 hours	○	○	○	○	○	○	○	○	○
		1500 hours	○	○	○	○	○	○	○	×	×
	Weather resistance (0.2 mm thick)	500 hours	○	○	○	○	○	○	○	○	○
		1000 hours	○	○	○	○	○	○	○	×	×
		1500 hours	△	△	△	△	△	△	△	×	×
	Workability 1		A	A	A	A	A	B	A	-	-

[0149]

(Example 8)

With respect to 100 parts of the polymer Pa, an age resister (Adekastab LA62, Adekastab LA67, or Irganox 1010), and a thixotropic agent (Disparlon #6500) were mixed and dispersed in the amounts in parts by mass indicated in Table 3, and a filler (Neolite SP-T or Whiton SB), from which moisture had been removed in advance by drying under heating, were added and mixed with the above mixture in the amounts in parts by mass indicated in Table 3. Furthermore, a macromolecular plasticizer (K1) and a dehydrating agent (VTMS) were added and mixed therewith in the amounts in parts by mass indicated in Table 3. Furthermore, an adhesiveness imparting agent (N-(2-aminoethyl)-3-aminopropyltrimethoxysilane or γ-glycidoxypropyltrimethoxysilane) and a curing catalyst (DBTDAA) were added thereto in the amounts in parts by mass

indicated in Table 3, and the mixture was mixed and debubbled. Subsequently, the mixture was filled in a cartridge for sealant which was capable of blocking the penetration of moisture in air, and thus a curable composition was obtained. Here, the abbreviations used for the raw materials of the curable composition in the Table 3 are marked with the symbol * and numeral references, and the details are indicated in Table 5.

[0150]

(Examples 9 to 14 and Comparative Examples 3 to 4)

Curable compositions of Examples 9 to 14 and Comparative Examples 3 to 4 were produced in the same manner as in the production method for the main agent of Example 8, with the raw materials and compositions (mass ratio) indicated in Table 3.

[0151]

[Table 3]

			Example							Comparative Example	
			8	9	10	11	12	13	14	3	4
Blend	Polymer	Pa	100	-	-	100	-	-	100	-	-
		Pb	-	100	-	-	100	-	-	100	-
		Pc	-	-	100	-	-	100	-	-	-
		P2	-	-	-	-	-	-	-	-	100
	Macromolecular plasticizer	K1	40	40	40	-	-	-	-	-	40
		K2	-	-	-	40	-	-	-	-	-
		K3	-	-	-	-	30	-	-	-	-
		K4	-	-	-	-	-	40	-	-	-
		K5*1	-	-	-	-	-	-	40	-	-
	Low molecular weight plasticizer	DOP*2	-	-	-	-	10	-	-	40	-
	Filler	Neolite SP-T*4	75	75	75	75	75	75	75	75	75
		Whiton SB*5	75	75	75	75	75	75	75	75	75
	Thixotropic agent	Disparlon #6500*23	3	3	3	3	3	3	3	3	3
	Adhesiveness imparting agent	Silane compound*24	1	1	1	2	-	-	1	1	1
		Silane compound*25	-	-	-	-	2	2	-	-	-
		Silane compound*26	1	1	1	-	1	1	1	1	1
	Dehydrating agent	VTMS*27	3	3	3	-	3	-	3	3	3
		TES*28	-	-	-	3	-	3	-	-	-

Age resister	Adekastab LA62[*17]	1	1	1	0.5	-	1	1	1	1
	Adekastab LA67[*18]	-	-	-	0.5	1	-	-	-	-
	Tinuvin 327[*19]	1	1	1	1	1	1	1	1	1
	Irganox 1010[*20]	1	1	1	1	1	1	1	1	1
Curing catalyst	DBTDAA[*29]	1	1	1	-	-	-	1	1	1
	DBTO/AA[*30]	-	-	-	1	-	1	-	-	-
	DBTDL[*31]	-	-	-	-	1	-	-	-	-

[0152]

Each of the compositions obtained in Examples 8 to 14 and Comparative Examples 3 to 4 was extruded out from the cartridge using a cartridge gun, and was applied on a 1 mm-thick aluminum plate to a thickness of 5 mm. The composition was cured for 7 days at 20°C and at a humidity of 65% to form a cured product having a thickness of 5 mm on the aluminum plate. This was used as a test specimen. This specimen was subjected to a weathering test with a Sunshine Super Long Life Weather Meter (manufactured by Suga Test Instruments Co., Ltd.), and the surface conditions of the test specimen after 500 hours, after 1000 hours and after 1500 hours were observed. The evaluation was based on the following criteria: ○: no cracks are recognized, △: slight thin cracks are recognized, and ×: obvious cracks are recognized.

[0153]

Subsequently, each of the compositions obtained Examples 8 to 14 and Comparative Examples 3 to 4, respectively, was applied on a 1 mm-thick aluminum plate to a thickness of 0.2 mm, and the composition was cured for 7 days at 20°C and at a humidity of 65% to form a cured product having a thickness of 0.2 mm on the aluminum plate. This was used as a test specimen.

This specimen was subjected to a weathering test with a Sunshine Super Long Life Weather Meter (manufactured by Suga Test Instruments Co., Ltd.), and the surface conditions of the test specimen after 500 hours and after 1000 hours were observed. The evaluation was based on the following criteria: ○: whitening is not recognized, △: slight whitening (discoloration) is recognized, and ×: whitening (discoloration) is clearly recognized.

[0154]

Furthermore, the workability condition at the time of extruding the curable compositions of Examples 8 to 14 from the cartridges using a cartridge gun, was evaluated based on three grades (workability 2). The evaluation was based on the following criteria: A: extrudable with light force, B: slight force required in the extruding, and C: significant force required in the extruding.

[0155]

The results of the above tests are summarized in the following Table 4. As it is obvious from the results indicated in Table 4, when the thickness was thick (thickness: 5 mm), the cured products of the curable compositions obtained in the Examples 8 to 14 were not recognized to have cracks at a time point when an exposure time of 1000 hours elapsed, and were recognized to have slight thin cracks at a time point when 1500 hours elapsed, thus exhibiting satisfactory weather resistance over a long time. On the other hand, the cured products of the curable compositions obtained in the Comparative Examples 3 to

4 generated cracks at a time point between exposure times of 500 hours and 1000 hours, for the same thickness.

[0156]

When the thickness was thin (thickness: 0.2 mm), the cured products of the curable compositions obtained in the Examples 8 to 14 were not at all recognized to have whitening at a time point when an exposure time of 1000 hours elapsed, and were recognized to have slight whitening (discoloration) at a time point when an exposure time of 1500 hours elapsed. On the other hand, the cured products of the curable compositions obtained in the Comparative Examples 3 to 4 had whitening occurred at a time point between exposure times of 500 hours and 1000 hours, for the same thickness.

[0157]

It was also shown that all of the curable compositions obtained in the Examples 8 to 14 exhibited satisfactory workability upon being extruded from the cartridge using a cartridge gun.

[0158]

[Table 4]

			Example							Comparative Example	
			8	9	10	11	12	13	14	3	4
Test results	Weather resistance (5 mm thick)	500 hours	○	○	○	○	○	○	○	○	○
		1000 hours	○	○	○	○	○	○	○	×	×
		1500 hours	△	△	△	△	△	△	△	×	×
	Weather resistance (0.2 mm thick)	500 hours	○	○	○	○	○	○	○	○	○
		1000 hours	○	○	○	○	○	○	○	×	×
	Workability 2		A	A	A	A	A	B	A	-	-

[0159]

[Table 5]

Numeral reference	Chemical species
*1	L-3000 (polytetramethylene glycol having a molecular weight of about 3000, manufactured by Hodogaya Chemical Co., Ltd.; viscosity at 25°C: 4.5 Pa·s)
*2	Di-2-ethylhexyl phthalate
*3	Di(2-ethylhexyl) 4,5-epoxycyclohexane-1,2-dicarboxylate
*4	Colloidal calcium carbonate (manufactured by Takehara Industrial Chemical Corp.)
*5	Heavy calcium carbonate (manufactured by Shiraishi Calcium Kaisha, Ltd.)
*6	Q-CEL 520 (the PQ Corp.)
*7	UCAR PHENOLIC MICROBALLOONS BJO-0930 (manufactured by Union Carbide Corp.)
*8	MATSUMOTO MICROSPHERE MFL-100CA (manufactured by Matsumoto Yushi-Seiyaku Co., Ltd.)
*9	EXPANCEL 461DE (manufactured by Nippon Fillite Kabushiki Kaisha)
*10	Hydrogenated castor oil (manufactured by Kusumoto Chemicals, Ltd.)
*11	Trimethyl silyl ether of trimethylolpropane
*12	2-Ethylhexyloxytrimethylsilane
*13	Phenyloxytrimethylsilane
*14	Hexamethyldisilazane
*15	Trimethylolpropane trisacrylate (manufactured by Toagosei Co., Ltd.)
*16	Bisphenol A type epoxy resin (manufactured by Yuka Shell Epoxy Co., Ltd.)
*17	Hindered amine-based photostabilizer (manufactured by Asahi Denka Co., Ltd.)
*18	Hindered amine-based photostabilizer (manufactured by Asahi Denka Co., Ltd.)
*19	Benzotriazole-based photostabilizer (manufactured by Ciba Specialty Chemicals Corp.)
*20	Hindered phenol-based antioxidant (manufactured by Ciba Specialty chemicals Corp.)
*21	Mixture and reaction product of tin 2-ethylhexanoate/laurylamine at 3:1
*22	Kaolin (manufactured by Tsuchiya Kaolin Industry, Ltd.)
*23	Fatty acid amide (manufactured by Kusumoto Chemicals, Ltd.)
*24	N-(2-aminoethyl)-3-aminopropyltrimethoxysilane
*25	N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane
*26	γ-Glycidoxypropyltrimethoxysilane
*27	Vinyltrimethoxysilane
*28	Tetraethoxysilane
*29	Dibutyltin bisacetylacetonate
*30	Reaction product of dibutyltin oxide and acetic acid
*31	Dibutyltin dilaurate

[0160]

[Effects of the Invention]

As discussed above, according to the present invention, it is possible to provide a curable composition which is capable of more certainly preventing the generation of cracks,

whitening or the like over a long time, irrespective of whether the cured product is a thick film or a thin film.